Analytical Feasibility Support Document for the Six-Year Review of Existing National Primary Drinking Water Regulations

(Reassessment of Feasibility for Chemical Contaminants)

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United States Environmental Protection Agency
Office of Water
Office of Ground Water and Drinking Water
Standards and Risk Management Division
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This report is issued in support of the preliminary revise/not revise decisions for the Six-Year Review Notice of Intent. It is intended for public comment and does not represent final agency policy. EPA expects to issue a final version of this report with the publication of the final notice in 2002, reflecting corrections due to public comment on the preliminary notice and the supporting documents.

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(1) developing and/or reviewing the process used to assess whether the feasible limits have changed for a subset of the 68 chemical SDWA analytes under review;
(2) review and comment on the preliminary results;
(3) general QA/QC to verify that the approved analytical methods and the method detection limits listed for each contaminant was correct; and/or
(4) writing and editorial review of portions of this document.

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EPA also appreciates the technical support provided by The Cadmus Group, Inc, the prime contractor for this project. Dr. George Hallberg served as the Cadmus project manager and major contributions by Wendy Chou, Ashton Koo and Anne Isham are gratefully acknowledged. Their support in the development of this document included documentation of approved analytical methods and their MDLs, the analyses of the Water Supply Data, the development of the graphs and tables, a large portion of the writing in the results section, and general QA/QC of the analyses and the document.

Executive Summary

The Safe Drinking Water Act (SDWA), as amended in 1996, requires the Environmental Protection Agency (EPA) to review and revise, if appropriate, existing National Primary Drinking Water Regulations (NPDWRs). As part of the review, EPA developed a protocol document (entitled *EPA Protocol for the Review of Existing National Primary Drinking Water Regulations*) to describe the process and strategy for regulatory review that EPA used to meet its statutory requirement. EPA developed the protocol based on recommendations from the National Drinking Water Advisory Council (NDWAC), through internal Agency deliberations, and through discussions with the diverse stakeholders involved in drinking water and its protection. Based on the NDWAC recommendations, EPA's review included the consideration of five key elements, as appropriate: *health effects, analytical and treatment feasibility, implementation-related issues, occurrence and exposure, and economic impacts*. The purpose of the analytical methods feasibility analysis was to determine whether changes in the practical quantitation level (PQL) were possible in those instances where the Maximum Contaminant Level is limited, or might be limited, by analytical feasibility. This document, "*Analytical Feasibility Support Document for the Six-Year Review of Existing National Primary Drinking Water Regulations: Reassessment of Feasibility for Chemical Contaminants*," describes the process recommended by NDWAC and used by EPA to address the analytical feasibility aspect of the current (1996-2002) Six-Year Review.

To be consistent with the accepted policy and procedures used by EPA to derive quantitation levels for drinking water contaminants, the Six-Year Review focused on the process that has been used by the Office of Ground Water and Drinking Water for many years. Historically, EPA's OGWDW used two main approaches to determine practical quantitation levels (PQLs) for SDWA analytes. One approach (and the preferred approach) used data from Water Supply (WS) Performance Evaluation (PE) studies. Although the primary use of the WS-PE data was for EPA's laboratory certification, the data were also used as a secondary data source for many years to develop PQLs when the spike concentrations were in the appropriate concentration range. The derivation of the PQL using WS data involved determining the concentration of an analyte at which 75 percent of EPA Regional and State laboratories achieved results within a specified range around the spike value. In the absence of WS data, the other approach that EPA used was the MDL multiplier method. In this approach, the PQL was calculated by multiplying the EPA-derived MDL by a factor of 5 or 10. The MDL multiplier method was mostly used in the early years of rule development for NPDWRs when insufficient WS data were available. Once sufficient WS data became available, most of the PQLs developed using the MDL multiplier were validated using WS data.

For the Six-Year analytical feasibility review, EPA focused on assessing whether the practical quantitation level has changed since promulgation for a subset of the 68 chemical NPDWRs. EPA performed the analytical feasibility analysis for a total of 38 NPDWRs that fell into one of two categories:

- First, for those contaminants where the MCL is currently limited by analytical feasibility (i.e., the MCL is set at the PQL) and the MCLG is still appropriate, EPA evaluated the currently approved methods for those contaminants and available WS data to determine whether it might be possible to lower the PQL and hence set an MCL that is closer to the MCLG.

whether it might be possible to lower the PQL and hence set an MCL that is closer to the MCLG.

- The second circumstance under which EPA re-evaluated the PQL was for contaminants identified under the Six-Year health effects technical review as having potential changes to their MCLG. Because the information for the health effects review was not completely available at the time the analytical methods analysis began, EPA took a broad-brush approach and included a number of contaminants that may not have needed a reassessment of their analytical feasibility.

For each of these 38 chemical NPDWRs, the analytical feasibility reassessment included:

(1) a *methods comparison* step to help identify whether the ability to detect (and therefore quantify) these contaminants at lower levels has increased;

(2) a *methods usage over time* step to identify the analytical methods that appear to be the most widely used for the analysis of particular contaminants.

(3) a *Water Supply data analysis* step to determine if a PQL can be recalculated (if sufficient WS information is available) or if there is an indication that a PQL may be lower using the available information.

The results of these three steps aided in assessing whether a PQL might change for a specific contaminant and, if so, estimating what the new PQL might be.

The results of Six-Year analytical feasibility review concluded that the majority of the available WS data were insufficient to actually recalculate the PQL for many of the 38 contaminants of interest. The data were considered insufficient because either the true value of the spike concentrations used in the WS studies were above the concentration of interest and/or the percentages of labs passing exceeded the 75 percent criterion used to calculate a PQL. However, for many of the 38 contaminants, the available data were sufficient to indicate whether the PQL might change or if the current PQL is still appropriate. Of the 38 NPDWRs evaluated, the available information indicates that the PQL for 23 might possibly be lower. The PQL for the remaining 15 appears to still be appropriate. For the 23 analytes where the WS data indicate that a lower PQL may exist, EPA used the information about method usage over time, the MDLs for these methods, and the 10 x MDL multiplier to estimate what the potentially lower PQL might be. This estimated value was used as a threshold value in the occurrence and exposure analyses to determine whether an improvement in public health protection might be possible if EPA were to consider gathering more definitive data to recalculate the PQL and possibly lower the MCL.

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I. Introduction

The Safe Drinking Water Act (SDWA), as amended in 1996, requires the Environmental Protection Agency (EPA) to review and revise, if appropriate, existing National Primary Drinking Water Regulations (NPDWRs). As part of the review, EPA developed a protocol document *(EPA Protocol for the Review of Existing National Primary Drinking Water Regulations)* that describes the process and strategy EPA used to review existing NPDWRs in order to meet its statutory requirement. EPA developed the protocol document based on recommendations from the National Drinking Water Advisory Council (NDWAC), through internal Agency deliberations, and through discussions with the diverse stakeholders involved in drinking water and its protection. To more efficiently utilize limited resources, EPA performed a series of analyses that were intended to target those NPDWRs that are the most appropriate candidates for revision. As part of the review, and where appropriate, EPA reviewed the following key technical elements to make decisions regarding regulatory changes: health risks assessments; technology assessments (analytical feasibility and treatment technology); other regulatory revisions (e.g., monitoring and reporting); occurrence and exposure analyses; and available economic information. This document discusses the analytical feasibility aspect of the current (1996-2002) Six-Year Review.

The 1999-2002 Six-Year Review includes the review of 68 chemical NPDWRs promulgated prior to the 1996 SDWA Amendments. Because the analytical measurement feasibility may have been the limiting factor in setting the Maximum Contaminant Level (MCL) for some of the existing NPDWRs or because the health effects reviews may indicate a potential change in the MCLG, this report examines the reassessment of analytical methods capabilities including a reassessment of whether the Practical Quantitation Levels (PQLs) may have changed since promulgation. The PQL is generally defined as "the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions" (50 FR 46906, November 13, 1985). The purpose of this support document is to:

- provide background information on the relationship between SDWA requirements and the analytical methods feasibility;
- describe how PQLs have historically been determined;
- and describe the process used to identify which of the 68 chemical NPDWRs under the 1996-2002 review are subject to a further assessment with regards to analytical methods capabilities and a reassessment of the PQL.

II. Background

A. What is the Relationship Between SDWA Requirements and Analytical Methods?

The SDWA [§1401(1)(C)(i); 42 U.S.C. § 300f(1)(C)(i)] states that an MCL for a national primary drinking water regulation is set "if, in the judgment of the Administrator, it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems." According to SDWA, NPDWRs include "criteria and procedures to assure a supply of drinking water which dependably complies with such maximum contaminant levels; including accepted methods of quality control and testing procedures to insure compliance with such levels" [§1401(1)(D); 42 U.S.C. § 300f(1)(D)]. Except in certain circumstances, EPA is to set the MCL as close to the Maximum Contaminant Level Goal (MCLG) as is feasible with the best available technologies (Section 1412 (b)(4)(B)). The MCLs for several SDWA contaminants were set due to the limits of the analytical feasibility at that time. Since the promulgation of pre-1996 SDWA NPDWRs, newer analytical methods and updated methods for measuring SDWA contaminants have been approved. The approval of newer analytical techniques may have provided laboratories with the analytical capability to measure some contaminants at lower levels. In addition, some laboratories may have improved in their ability to measure at lower levels using the same methods that were originally promulgated.

In considering analytical methods for use in compliance monitoring, EPA evaluates the overall sensitivity of the techniques. In previous regulations, EPA used two measures of analytical capability, the Method Detection Limit (MDL) and the Practical Quantitation Level (PQL).

- The MDL is a measure of method sensitivity. The MDL is defined at 40 CFR Part 136 Appendix B as *"the minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero."* MDLs can be operator, method, laboratory, and matrix-specific. Due to normal day-to-day and run-to-run analytical variability, MDLs may not be reproducible within a laboratory or between laboratories. The regulatory significance of the MDL is that EPA uses the MDL to determine when a contaminant is deemed to be detected and it can be used to calculate a PQL for that contaminant.

- In the preamble to a November 13, 1985 rulemaking (50 FR 46906), the PQL was defined as *"the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions."* The Agency has used the PQL to estimate or evaluate the minimum concentration at which most laboratories can be expected to reliably measure a specific chemical contaminant during day-to-day analyses of drinking water samples. The PQL is a means of integrating information on the performance of the approved analytical methods into the development of a drinking water regulation (52 FR 25699, July 8, 1987). The PQL incorporates the following (50 FR 46880, November 13, 1985; 52 FR 25690, July 8, 1987; 54 FR 22062, May 22, 1989):

    - quantitation,
    - precision and bias,
    - normal operations of a laboratory, and

- the fundamental need to have a sufficient number of laboratories available to conduct compliance monitoring analyses.

In some cases, the quantitation limit for a particular analyte may have been the limiting factor in the determination of the MCL for that analyte. This could be especially true for contaminants with MCLGs of zero. Also, there are several SDWA contaminants with non-zero MCLGs that have their MCL set at the PQL.

B. How Have PQLs Been Determined in the Past for SDWA Contaminants?

Historically, EPA's OGWDW used two main approaches to determine a PQL for SDWA analytes. One approach (and the preferred approach) used data from Water Supply (WS) Performance Evaluation (PE) studies. Although the primary use of the WS-PE data was for EPA's laboratory certification, the data were also used as a secondary data source for many years to develop PQLs when the spike concentrations were in the appropriate concentration range. The derivation of the PQL using WS data involved determining the concentration of an analyte at which 75 percent of EPA Regional and State laboratories achieved results within a specified range around the spike value. In the absence of WS data, the other approach that EPA used was the MDL multiplier method. In this approach, the PQL was calculated by multiplying the EPA-derived MDL by a factor of 5 or 10. The 5 or 10 multiplier was used to account for the variability and uncertainty that can occur at the MDL. The MDL multiplier method was mostly used in the early years of rule development for NPDWRs when insufficient WS data were available. Once sufficient WS data became available, most of the PQLs that were developed using the MDL multiplier were validated using WS data.

1. How Were Water Supply Studies Conducted?

Water Supply Performance Evaluation (WS PE) studies were an integral part of EPA's certification program for drinking water laboratories for over 20 years. Historically, WS studies were conducted semi-annually by EPA for all current and proposed drinking water contaminants. Although the WS studies were conducted semi-annually, for certification purposes, laboratories were only required to demonstrate acceptable performance once a year (141.23(k)(3) and 141.24(f)(17)). WS study samples (spike samples) were sent to all laboratories that conduct drinking water analyses, including utility laboratories, commercial laboratories, and State and EPA Regional laboratories. Each WS study included samples or sample concentrates that were analyzed both for all SDWA analytes and for analytes that were being considered for regulation under the SDWA.

During these WS studies, EPA's National Exposure Research Laboratory (NERL) in Cincinnati, Ohio, sent participating laboratories a set of stable sample concentrates in sealed glass ampules, a data reporting form, and appropriate instructions. Each laboratory produced the study samples by diluting a measured quantity of the specific concentrates to volume with reagent water. The laboratory then analyzed the samples using the specified procedures. The completed reporting form was sent to EPA for evaluation, the data were carefully reviewed (QA/QC'ed), entered into a database, and a fully detailed report was then returned to each laboratory. The responsible State or EPA office contacted those laboratories that demonstrated potential problems.

At this point in time, the WS Performance Evaluation studies are no longer performed by EPA. On July 18, 1996 (61 FR 37464), EPA proposed options for the externalization of the PE studies program (now referred to as the Proficiency Testing or PT program). After evaluating public comment, in the June 12, 1997 final notice EPA stated that the Agency has decided (62 FR 32112):

> *...on a program where EPA would issue standards for the operation of the program, the National Institute of Standards and Technology (NIST) would develop standards for private sector PE (PT) suppliers and would evaluate and accredit PE suppliers, and the private sector would develop and manufacture PE (PT) materials and conduct PE (PT) studies. In addition, as part of the program, the PE (PT) providers would report the results of the studies to the study participants and to those organizations that have responsibility for administering programs supported by the studies.*

Since the last WS PE studies performed by EPA were done in the Fall of 1999, the externalization of the PE program should not effect the data needed for this Six-Year Review process. However, at this time the Agency has not determined how to gather data to reassess PQLs for subsequent reviews of NPDWRs.

2. What Criteria Are Used to Determine a PQL?

The derivation of the PQL involves determining the concentration of an analyte at which a set percentage of the laboratories achieve results within a specified range of the spiked value. Historically, the percentage of laboratories has been set at 75 percent, while a range of acceptance limits around the spiked value has been used. In many cases, EPA derived PQLs only from the data submitted by the EPA Regional and State laboratories that participate in the WS studies.

A PQL derived from WS data in such a manner is considered a stringent target for routine laboratory performance because:

- WS samples are prepared in reagent water and therefore do not contain the matrix interferences that may occur in field samples.
- Laboratories analyze only a small number of samples for the study and are aware that the samples are for the purposes of performance evaluation (i.e., they are not "blind" samples).

In deriving a PQL from WS study data, the Agency typically sets a fixed percentage or 2 sigma (2 standard deviation) acceptance window around the known concentration (or spike value) of the WS samples. Then the percentage of laboratories achieving results within the specified acceptance window (y-axis) is plotted against the known spike concentration of the Water Supply study samples (x-axis). While the acceptance limits for inorganics typically range from 15 to 30 percent (40 CFR §141.23(k)(3)(ii)), the acceptance limits for organics generally range from 20 to 50 percent (141.24(f)(17)(i) and 40 CFR §141.24(h)(19)(i)). Several SDWA analytes have acceptance limits of 2 sigma (2 standard deviation). Linear regression or graphical analysis is performed on the WS data to determine the concentration at which 75 percent of EPA Regional and State laboratories achieve acceptable results.

III. How Did EPA Identify Which Contaminants to Evaluate for a PQL Reassessment?

For the Six-Year analytical feasibility review, EPA focused on assessing whether the practical quantitation level (or PQL) has changed since promulgation for a subset of the 68 chemical NPDWRs. Figure 1 illustrates the overall Six-Year protocol and the basic process used to identify the subset of contaminants for which a PQL reassessment should be appropriate. Using the protocol, EPA identified and performed the analytical feasibility analysis for a total of 38 NPDWRs (Table 1), which fell into one of two categories:

- First, for those contaminants where the MCL is currently limited by analytical feasibility (i.e., the MCL is set at the PQL) and the MCLG is still appropriate, EPA evaluated the currently approved methods for those contaminants and available WS data to determine whether it might be possible to lower the PQL and hence set an MCL that is closer to the MCLG.

- The second circumstance under which EPA re-evaluated the PQL was for contaminants identified under the Six-Year health effects technical review as having potential changes to their MCLG. Because the information for the health effects review was not completely available at the time the analytical methods analysis began, EPA took a broad-brush approach and included a number of contaminants that may not have needed a reassessment of their analytical feasibility.

Figure 1. Overview of the Protocol for the Revise/Not Revise Decision with a Focus on Where Analytical Feasibility was Re-evaluated.

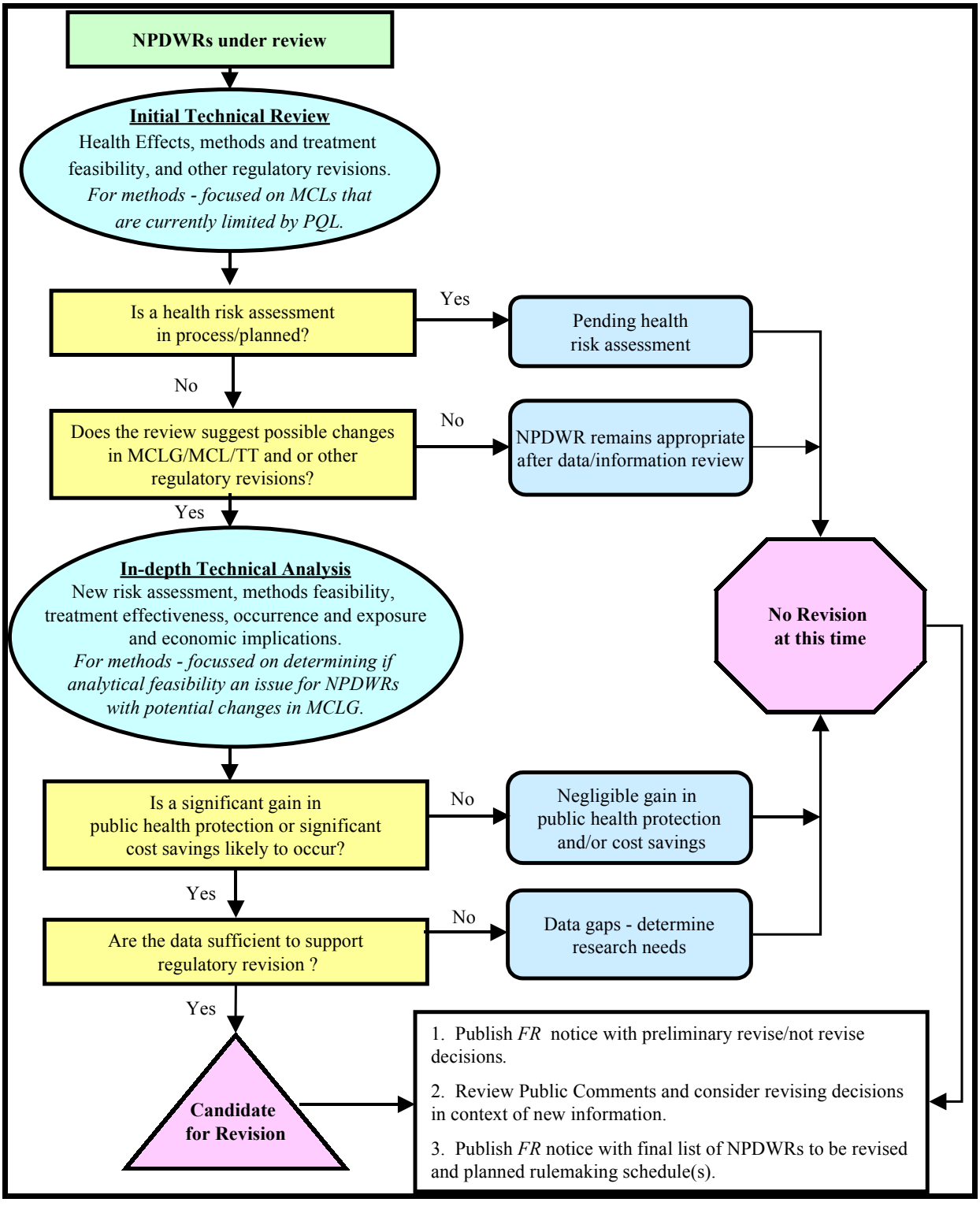


Table 1. SDWA Chemical Contaminants Undergoing Analytical Methods/PQL Reassessment

	SDWA Chemical Contaminant	MCLG [1] (mg/L)	MCL [2] (mg/L)	Current PQL [3,4] (mg/L)	Acceptance Limit [5]
1	Alachlor	zero	0.002	0.002	± 45 %
2	Benzene	zero	0.005	0.005	± 20 % or 40 %
3	Benzo(a)pyrene	zero	0.0002	0.0002	2 Std Dev.
4	Beryllium	0.004	0.004	0.001	± 15 %
5	Bis(2-ethylhexyl)phthalate	zero	0.006	0.006	2 Std Dev
6	Cadmium	0.005	0.005	0.002	± 20 %
7	Carbofuran	0.04	0.04	0007	± 45 %
8	Carbon tetrachloride	zero	0.005	0.005	± 20 % or 40 %
9	Chlordane	zero	0.002	0.002	0.45
10	Chromium (total - Cr III and VI)	0.1	0.1	0.01	± 15 %
11	1,2-Dibromo-3-chloropropane (DBCP)	zero	0.0002	0.0002	± 40 %
12	1,4-Dichlorobenzene (para)	0.075	0.075	0.005	± 20% or 40 %
13	1,2-dichloroethane	zero	0.005	0.005	± 20% or 40 %
14	1,1-dichloroethylene	0.007	0.007	0.005	± 20% or 40 %
15	Dichloromethane (methylene chloride)	zero	0.005	0.005	± 20% or 40 %
16	1,2- Dichloropropane	zero	0.005	0.005	± 20% or 40 %
17	Dioxin (2,3,7,8-TCDD)	zero	3×10^{-8}	3×10^{-8}	2 Std Dev
18	Diquat	0.02	0.02	0.004	2 Std Dev
19	Ethylene dibromide	zero	0.00005	0.00005	± 40 %
20	Fluoride	4.0	4.0	0.5	± 10 %
21	Glyphosate	0.7	0.7	0.06	2 Std Dev
22	Heptachlor	zero	0.0004	0.0004	± 45 %
23	Heptachlor epoxide	zero	0.0002	0.0002	± 45 %
24	Hexachlorobenzene	zero	0.001	0.001	2 Std Dev
25	Hexachlorocyclopentadiene	0.05	0.05	0.001	2 Std Dev
26	Mercury	0.002	0.002	0.005	± 30 %
27	Methoxychlor	0.04	0.04	0.01	± 45 %

	SDWA Chemical Contaminant	MCLG [1] (mg/L)	MCL [2] (mg/L)	Current PQL [3,4] (mg/L)	Acceptance Limit [5]
28	Oxamyl (Vydate)	0.2	0.2	0.02	2 Std Dev19
29	PCBs - Polychlorinated biphenyls (as decachlorobiphenyl)	zero	0.0005	0.0005	0 to 200 %
30	Pentachlorophenol	zero	0.001	0.001	± 50 %
31	Picloram	0.5	0.5	0.001	2 Std Dev
32	Tetrachloroethylene	zero	0.005	0.005	± 20% or 40 %
33	Thallium	0.0005	0.002	0.002	0.3
34	Toxaphene	zero	0.003	0.003	± 45%
35	1,1,1-Trichloroethane	0.2	0.2	0.005	± 20% or 40 %
36	1,1,2-Trichloroethane	0.003	0.005	0.005	± 20% or 40 %
37	Trichloroethylene	zero	0.005	0.005	± 20% or 40 %
38	Vinyl chloride	zero	0.002	0.002	± 40%

Footnotes:
1. The MCLGs for inorganics are listed at 40 CFR 141.51. The MCLGs for organics are listed at 40 CFR 141.50.
2. The MCLs for inorganics are listed at 40 CFR 141.62. The MCLs for organics are listed at 40 CFR 141.61.
3. The PQL for fluoride is published in 51 FR 11397 (April 1986). The PQLs for benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1-trichloroethane and vinyl chloride are published in 52 FR 25690 at 25700 (July 8, 1987). The PQLs for alachlor, cadmium, carbofuran, chlordane, chromium, 1,2-dibromo-3-chloropropane, 1,2-dichloropropane, heptachlor, heptachlor epoxide, ethylene dibromide, mercury, methoxychlor, PCBs, pentachlorophenol, tetrachloroethylene, and toxaphene are published in 56 FR3526 at 3552 (January 30, 1991). In this FR the PQL for pentachlorophenol was proposed but the final PQL was published in 56 FR 30266 (July 1, 1991) at 30270. The PQL for beryllium, benzo(a)pyrene, bis or di(2-ethylhexyl)phthalate dichloromethane, dioxin, diquat, glyphosate, hexachlorobenzene, hexachlorocyclopentadiene, picloram and thallium 1,1,1-trichloroethane are published in 57 FR 31776 at 31801 (July 17, 1992).
4. The acceptance limits inorganic can be found at CFR 141.23(k)(3)(ii). Acceptance limits for the organic chemicals are found at CFR 141.24(f)(17)(i)(C and D) and CFR 141.24(h)(19)(i)(B).

IV. What Approaches Were Used to Reassess the PQLs of Contaminants Identified by the Six-Year Review Process?

For this Six-Year Review process, several approaches could be used for the reassessment or re-evaluation of the PQLs for selected chemical contaminants. However, to be consistent with the policies and the process that the Agency has used in the past (50 FR 46880, November 13, 1985; 52 FR 25690, July 8, 1987; 54 FR 22062, May 22, 1989), only the "WS data" and the "MDL Multiplier" approaches were considered for the Six-Year Review process. Of these two approaches, the WS data approach is the preferred route since it relies on actual data to determine the level of quantitation. For the Six-Year Review, the MDL multiplier method is only used to estimate what a potential PQL could be if WS data are sufficient to indicate a change but insufficient to actually recalculate a PQL. There are advantages and disadvantages for each of

these approaches. Some of the advantages and disadvantages for these PQL derivation approaches are as follows:

(1) *Analysis of WS PE Data* - Uses data from WS studies to derive a new PQL. This value is compared to the old PQL (i.e., the one that is currently in place).

The advantages of the WS PE Data methods of deriving a PQL -

- Uses inter-laboratory data collected at concentrations near the MCL.
- More representative of what methods are being used for the analysis of that contaminant.
- May be the preferred approach for contaminants with MCLGs of zero.

The disadvantages of the WS analysis method of deriving a PQL -

- In the past, some stakeholders have felt that the PQL may be influenced by the set of WS data used (i.e., using data from all laboratories as opposed to only using data from EPA State and Regional laboratories).

- Some stakeholders have felt that the laboratory performance on WS data may be skewed, because WS samples may be treated as special samples that are critical for laboratory certification.

- The derivation of PQLs from WS data is a resource- and time-intensive process.

- Because the WS samples are designed to test precision and accuracy around the MCL, the WS data may not cover concentrations several orders of magnitude below the current MCL. Hence, for some analytes, data points at lower levels may not be represented.

(2) *The MDL-Multiplier Approach* - Using the MDL of the currently approved method(s) for each contaminant, the 5 or 10 multiplier method can be used to estimate the PQL. This value is then compared to the PQL that was derived before the 1996 SDWA Amendments.

The advantage of the MDL multiplier approach - it is a relatively easy and clear process.

The disadvantages of the MDL multiplier approach -

- The WS studies test laboratory performance near the MCL as opposed to the MDL. A PQL derived from the MDL multiplier method may not be representative, because the reproducibility of a result obtained at the MDL is often not as good as that obtained near the MCL.

- Because several methods may be approved for the same contaminant, it can be difficult to decide which MDL to select for the PQL calculation. However, knowledge of the methods that are the most widely used can be determined from the WS data since laboratories report which method was used to analyze spike samples.

Acknowledging the advantages and disadvantages of the WS analysis and the MDL multiplier approach, EPA used the following steps for the Six Year Review to reassess analytical feasibility for the 38 chemical contaminants identified:

- The first step is the *methods comparison* step. This step compared the method detection limits of the analytical methods which were available at the time the PQL was set to the method detection limits for the currently approved analytical methods. This methods comparison should help to identify whether the ability to detect (and therefore quantify) these contaminants at lower levels has increased.

- The second step is the *method usage over time*. This step used information from the last eight Water Supply studies (WS 34 through WS 41; 1996 to 1999) to generate a bar graph of the distribution of the analytical methods used to analyze the spike samples in the WS studies. This analysis should give an idea of the analytical methods that appear to be the most widely used for the analysis of particular contaminants. Knowing which analytical methods are the most widely used and the MDL for these methods can aid in estimating where the quantitation may lie today.

- The third and last step is the *Water Supply data analysis* step. If Water Supply data are sufficient, more recent WS data can be used to recalculate the PQL (using linear regression or graphical analyses) and determine if the quantitation level has changed. Data may be considered insufficient if there are not enough data points around the 75 percent criteria to recalculate the PQL using linear regression or graphical analysis. This may occur if the laboratories evaluated exhibit high passing rates (>75 percent) for all of the WS studies evaluated and/or no WS spike samples were below the concentration of the current PQL. However, even if the WS data are insufficient to actually recalculate the PQL, the information may be useful to either confirm that the current PQL still appears to remain appropriate or it may give an indication as to whether the PQL is likely to change (if the data points at concentrations close to the current PQL are available).

Using the information from these three steps helped EPA to determine if our ability to quantify contaminants at lower levels has increased. If there was an indication that the PQL has or could change, then pending the results of the health effects and occurrence review, as well as risk management considerations, these chemical contaminants may be subject to a full blown PQL reassessment (i.e., gathering data that sufficiently covers the area around the 75 percent laboratory passing criteria and the appropriate concentration range).

Note: This document will not discuss whether a full blown PQL reassessment is necessary for specific contaminants. Instead, that decision will be made after the integration of these results with the health effects and occurrence and exposure reviews and discussed in the Six Year Notice of Intent.

V. Results of the PQL Reassessment

Alachlor

Results of the Method Comparison

The approved drinking water methods for the determination of alachlor, a Phase II synthetic organic compound (SOC), were listed in the 1991 NPDWRs (56 FR 3526). These methods all utilize GC or GC/MS with several extraction and/or detector variations: EPA Methods 505, 507, and 525.1. Since promulgation of these original methods, the Agency has eliminated EPA 525.1 from the list of approved methods, and has approved the use of three new GC methods: EPA Methods 508.1, 525.2, and 551.1. The three new methods are approximately 10 to 100 times more sensitive than the earlier methods. The current EPA 505 is nearly equivalent in sensitivity relative to the time of Phase II promulgation, whereas the current EPA 507 is about twice as sensitive. Table 2 summarizes the current and previous EPA methods along with their MDLs.

Table 2. Results of the Analytical Methods Comparison for Alachlor (Newly Promulgated Methods are Indicated in Bold)

MCL = 2 µg/L	**Current PQL = 2 µg/L**	**DL▲ = 0.2 µg/L**	**Acceptance Limit† = ± 45%**		
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	Microextraction, GC	0.225	EPA 505[2]	Microextraction, GC	0.223
EPA 507[1]	GC with NPD	0.38	EPA 507[2]	GC with ECD	0.14
EPA 525[1]	GC/MS with LSE	0.1	**EPA 508.1[2]**	GC with LSE, ECD	0.009
			EPA 525.2[2]	GC/MS with LSE	0.069 - 0.11*
			EPA 551.1[2]	GC/MS with LLE, ECD	0.005 - 0.025*

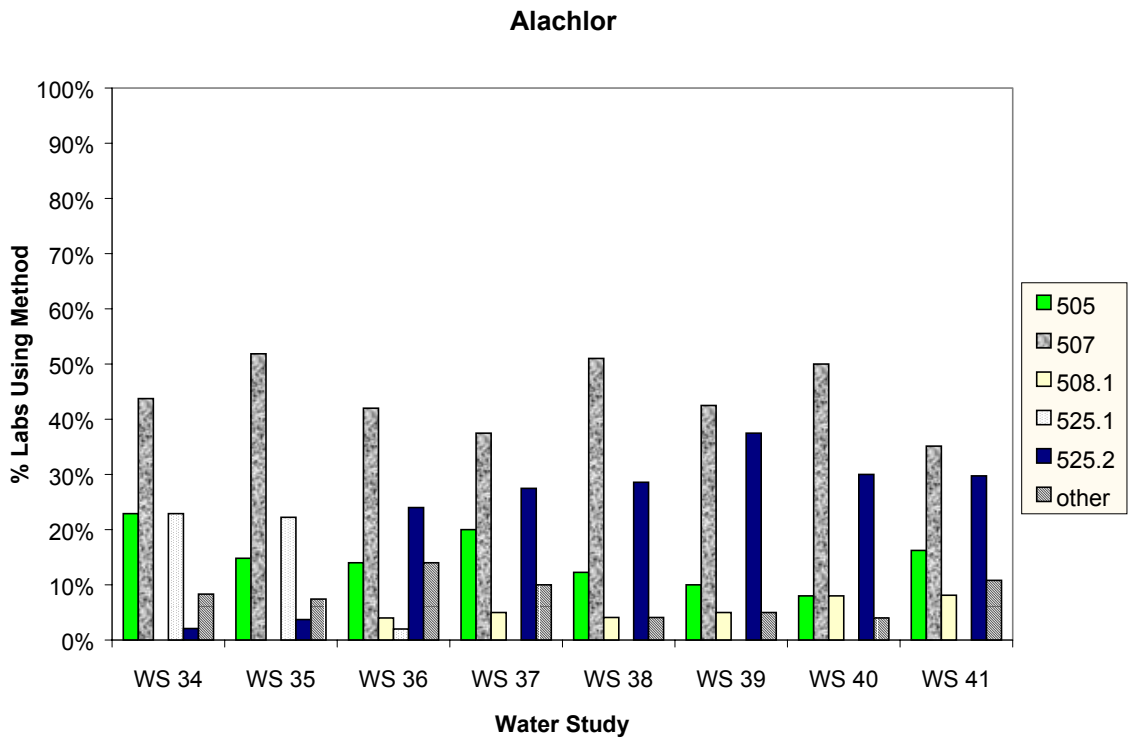
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).
†Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 2 plots the distribution of analytical techniques used by the EPA and State laboratories in WS 34 to 41. Methods categorized as "other" represent methods which were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 2, EPA 507 was used fairly consistently throughout WS 34 to 41. Use of EPA 525.1 was phased out after WS 36, while use of EPA 525.2 increased significantly during the same study. EPA Methods 508.1, 505, and "other" methods remained in use minimally throughout the study period.

Figure 2. Distribution of Analytical Techniques by WS Study: Alachlor



b. Results of the PQL Analysis

As PE data were not available at the time of the original PQL determination, the PQL of 2 µg/L was derived using a multiplier of 10 on the interlaboratory MDL (0.15 µg/L) based on a study conducted by the Environmental Monitoring and Support Laboratory in Cincinnati, Ohio (54 FR 22104). Data from WS 24 to 41 were used to attempt a PQL re-evaluation. Table 3 summarizes these data, indicating the study number, the true value (i.e., the spiked value) of the WS sample, the number of results from EPA and State laboratories, and the calculated

percentage of laboratories whose results successfully passed within designated acceptance limits for alachlor (specified in 40 CFR §141.24(h)(19)(i) to be ± 45 percent).

Table 3. Evaluation of Alachlor Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA Regional and State Labs	% Labs Passing ± 45% Acceptance Limits
24a	0.735	19	100
26b	0.933	20	95.0
29	1.59	14	71.4
25a	1.87	13	100
32	2.33	43	86.0
31	2.50	25	76.0
30	3.21	40	97.5
34	3.43	48	100
27	3.80	17	88.2
33	4.27	30	86.7
24b	4.53	19	100
37	4.87	40	85.0
35	5.27	27	96.3
26a	5.66	20	95.0
36	7.34	50	100
38	9.52	49	93.9
25b	9.80	13	100
41	12.9	37	100
39	14.8	40	97.5
40	17.7	50	90.0

The data from the available PE studies were not conducive to PQL re-evaluation, as the percentage of labs passing generally exceeded the standard 75 percent passing criterion needed to calculate the PQL using linear regression or graphical analysis (with the exception of one study - WS 29). However, even around the original PQL of 2 µg/L, the percentage of laboratories

passing is extremely variable and ranges from 71.4 percent in WS 29 (spike concentration = 1.59 µg/L) to 75 percent for WS 31 (spike concentration = 2.50 µg/L) to 100 percent for several WS studies at varying concentrations. Even at higher concentrations of 3.8 µg/L (WS 27) and 4.27 µg/L (WS 37) the laboratory passing rates dip to 88 and 87 percent, respectively. Based on this information, EPA believes the PQL for alachlor appears to still be in the appropriate range.

Conclusion for Alachlor

Since the promulgation of the 1991 NPDWR for alachlor and other Phase II SOCs, three new analytical methods (EPA Methods 525.2, 508.1, and 551.1) have been approved for the determination of alachlor in drinking water. All three new methods exhibit lower MDLs than the original methods. Based on the distribution of method use over time (Figure 2), it appears that EPA and State laboratories did not utilize the increased analytical sensitivity of the newer methods, instead preferring use of EPA 507. Meanwhile, a PQL for alachlor could not be recalculated using the PE data from WS 24 to 41. Nearly every study exhibited a laboratory success rate above the 75 percent criterion needed for re-evaluating the PQL, and furthermore, the range of true values generally exceeded the current PQL value. Therefore, the available PE data provide very limited evidence for revising the current PQL of 2 µg/L. However, based on the available data, EPA believes the PQL for alachlor is most likely in the appropriate range.

Benzene

Results of the Method Comparison

In July 1987, the final NPDWR for eight Phase I VOCs approved the use of EPA Methods 502.2, 503.1, 524.1, and 524.2 for the determination of benzene in drinking water (52 FR 25690). The currently approved methods for benzene determination are EPA Methods 502.2 and 524.2. Table 4 summarizes the MDLs for both the original and current approved versions of the methods. As compared to the original methods, the updated methods are equal in sensitivity to the original methods.

Table 4. Results of the Analytical Methods Comparison for Benzene

MCL = 5 µg/L Current PQL = 5 µg/L DL^ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL ◊ (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.2 [1]	Purge and Trap GC	0.01	EPA 502.2[2]	Purge and Trap GC	0.01
EPA 503.1 [1]	Purge and Trap GC	0.02	EPA 524.2[2]	GC/MS	0.03 - 0.04*
EPA 524.1 [1]	GC/MS	0.1			
EPA 524.2 [1]	GC/MS	0.04			

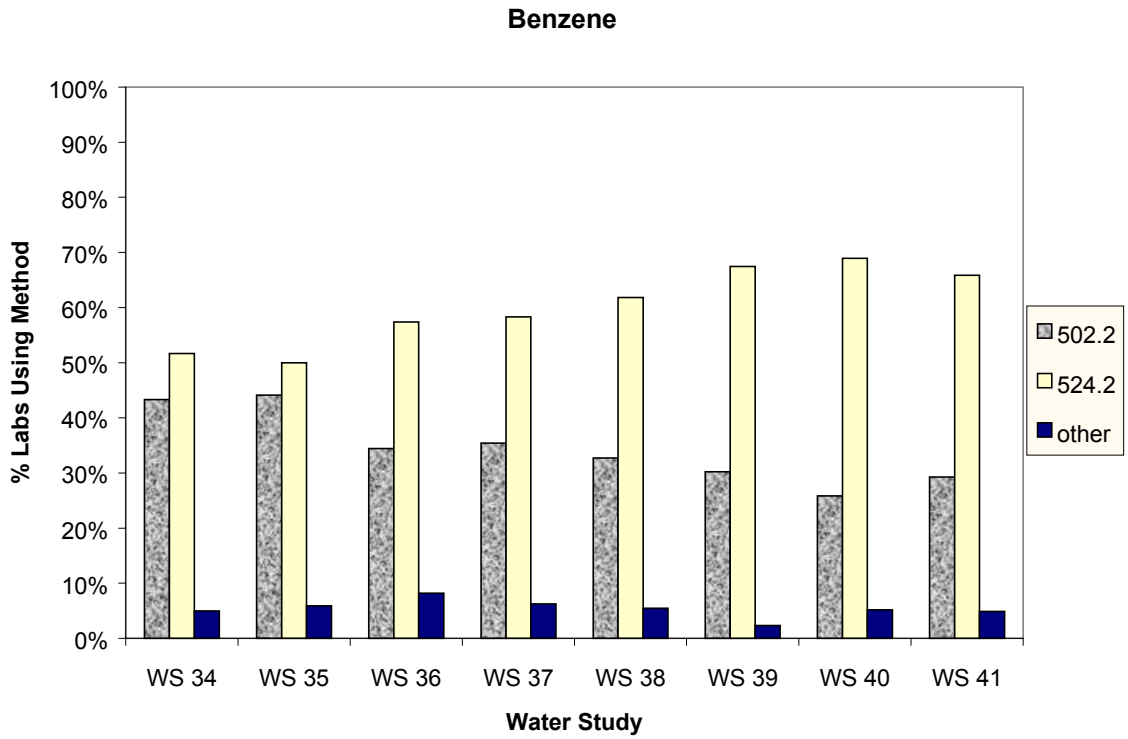
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for VOCs are listed at 40 CFR § 141.24(f)(17)(i).
† Acceptance limits for VOCs are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 3 summarizes the distribution of the different methods used by the EPA and State laboratories during WS studies 34 to 41. The category of "other" contains those methods that were either unknown or otherwise unidentified by the participating laboratories. As shown in Figure 3, use of EPA 524.2 during WS 34 to 41 generally increased over time while use of EPA 502.2 decreased very slightly during the same period. Overall, usage of EPA 524.2 remained consistently dominant over that of EPA 502.2. Use of the original EPA Methods, 503.1 and 524.1, were not apparent during this period.

Figure 3. Distribution of Analytical Techniques by WS Study: Benzene



b. Results of the PQL Analysis

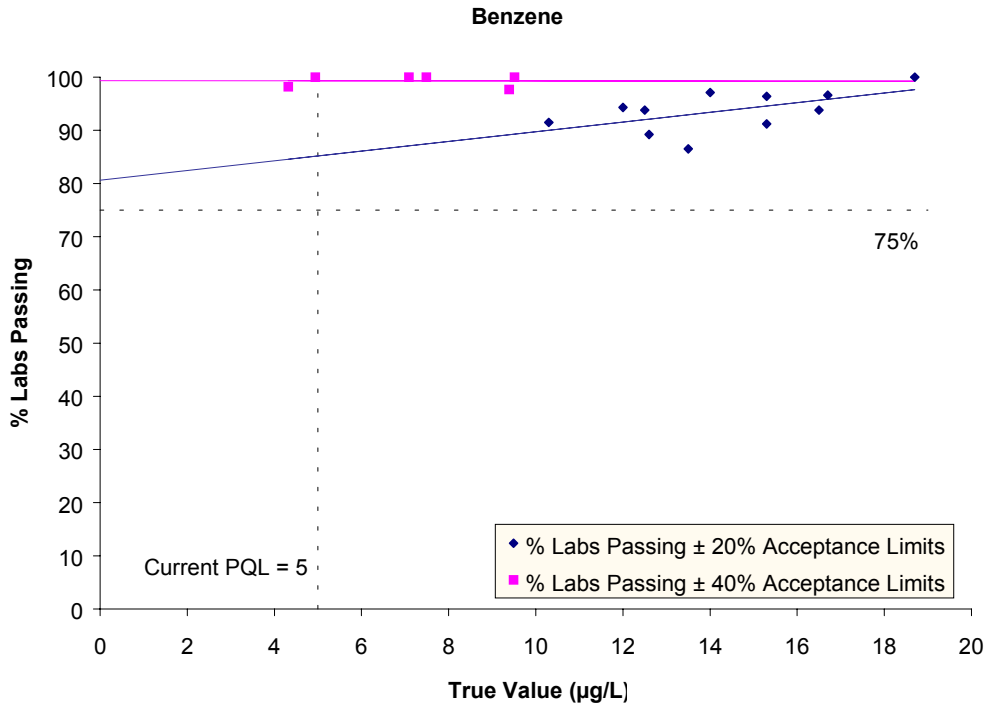
The original PQL of 5 µg/L for benzene was determined by multiplying the regulatory detection limit of 0.5 µg/L by a factor of 10 (52 FR 25700). To re-evaluate the PQL, multi-laboratory performance data from WS 24 through 41 were reviewed. Table 5 summarizes the results of these water studies, providing the study number, the spiked value for the WS sample, the number of laboratory results, and the percentage of laboratories whose reported results fell within the acceptance limits of ± 20 percent for true values greater than 10 µg/L and ± 40 percent for true values lower than 10 µg/L (specified at 141.24(f)(17)(i)).

Table 5. Evaluation of Benzene Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
24	4.32	57		98.2
34	4.94	60		100
27	7.09	38		100
36	7.49	61		100
39	9.39	43		97.7
30	9.51	60		100
26	10.3	59	91.5	
33	12.0	35	94.3	
37	12.5	48	93.8	
31	12.6	37	89.2	
25	13.5	37	86.5	
35	14.0	34	97.1	
29	15.3	34	91.2	
38	15.3	55	96.4	
32	16.5	65	93.8	
40	16.7	58	96.6	
41	18.7	41	100	

The overall data for benzene, as shown in Table 5, indicate that the passing rates for laboratories fall well above the 75 percent criterion for establishing a revised PQL value. However, as shown in Figure 4, the PE data for benzene display different relationships with true values concentration depending on the acceptance limits (20 or 40 percent). The data representing laboratories passing the 40 percent acceptance limits plot a horizontal line and do not contribute meaningfully to a PQL re-evaluation. For the laboratories passing the 20 percent acceptance limits, the regression line demonstrates a positive slope, although a PQL re-evaluation is also not possible because the true values exceed the current PQL. However, the high percentages of laboratories passing around the current PQL of 5 µg/L suggest that the PQL for benzene could possibly be lower.

Figure 4. Two-part Distribution of Benzene WS Data



Conclusion for Benzene

The method comparison results show that, since the promulgation of analytical methods under the original NPDWR for benzene, two of these methods are no longer approved for determination of this contaminant and method sensitivity has remained about the same. Evaluation of the quantitative PE data shows that the laboratories conducting WS analyses exhibited very high passing rates. Because the percentage of laboratories passing the PE testing exceeds the 75 percent criterion, a re-evaluation of the PQL could not be performed using this approach. But the high percentages of laboratories passing around the current PQL of 5 µg/L suggest that the PQL for benzene could possibly be lower.

Benzo(a)pyrene

Results of the Method Comparison

With the Phase V synthetic organic compounds (57 FR 31776), three approved methods were listed for determination of benzo(a)pyrene in drinking water, including gas chromatography/mass spectrometry (GC/MS) with liquid-solid extraction (LSE; EPA 525.1), high performance liquid chromatography (HPLC) with liquid-liquid extraction (LLE; EPA 550), and HPLC with LSE (EPA 550.1). Since this regulation was promulgated, the Agency has replaced the old GC/MS - LSE method with an updated version, EPA 525.2. As shown in Table 6, EPA 525.2 is estimated to be approximately 1.5 to 4 times more sensitive than the older methods in terms of its method detection level (MDL).

Table 6. Results of the Analytical Methods Comparison for Benzo(a)pyrene (Newly Promulgated Methods Indicated in Bold)

MCL = 0.2 µg/L	**Current PQL = 0.2 µg/L**		**DL▲ = 0.02 µg/L**	**Acceptance Limit† = ± 2xS.D.**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 525.1[1]	LSE, GC/MS	0.137	EPA 550[2]	LLE, HPLC	0.029
EPA 550[2]	LLE, HPLC	0.029	EPA 550.1[2]	LSE, HPLC	0.016
EPA 550.1[2]	LSE, HPLC	0.016	**EPA 525.2[3]**	LSE, GC/MS	0.032

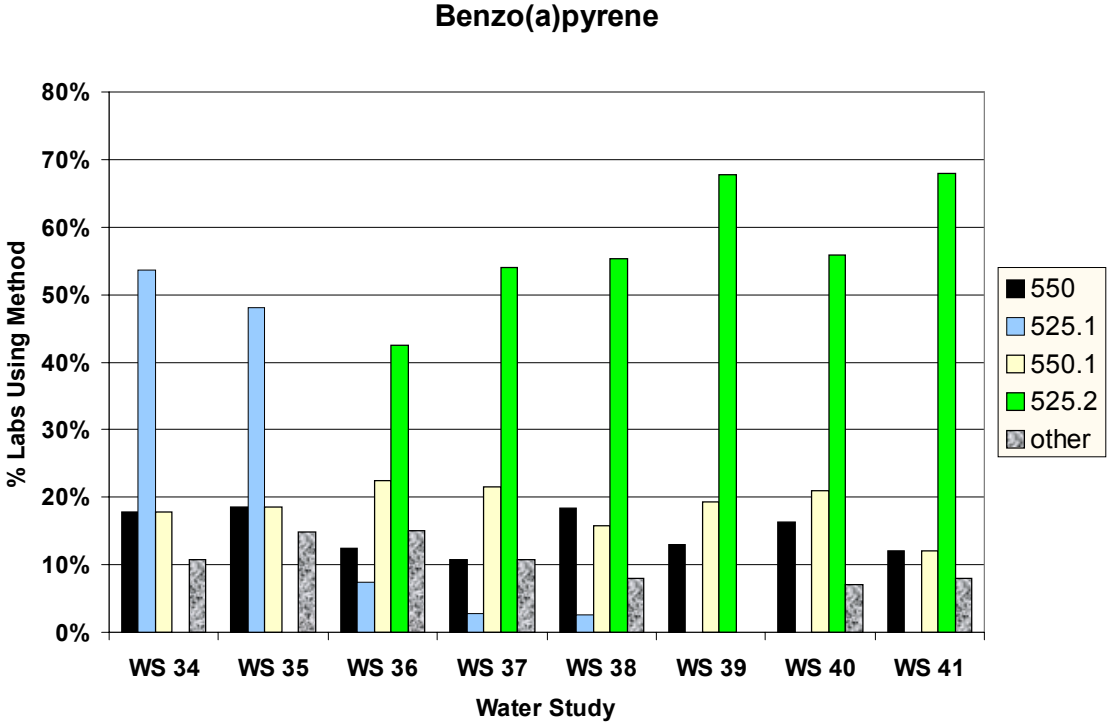
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Supplement I to Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-90/020, July 1990.
[3] "Supplement III to Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/R-95-131, August 1995.
▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).
† Acceptance limits are listed at 40 CFR §141.24(h)(19)(i).

Results of the WS Data Analysis

a. Method Usage Over Time

Figure 5 illustrates the distribution of the analytical techniques used by EPA and State laboratories in WS studies 34 to 41. The "other" techniques shown in this figure include unidentified, unknown, or unreported techniques. Figure 5 simply shows that, by the time of WS study 38, EPA 525.1 was almost completely phased out and replaced with EPA 525.2 (which, according to Table 6, is more sensitive).

Figure 5. Distribution of Analytical Techniques by WS Study: Benzo(a)pyrene



b. Results of the PQL Analysis

The original PQL was estimated at 0.2 µg/L (57 FR 31802) based on PE data compiled from WS studies 23, 24, 26, and 27. The data used for the re-evaluation of the PQL were taken from WS studies 24 through 41. Table 7 summarizes the results of these studies. The table provides the WS study number, the spiked or "true value" for the WS sample, the number of laboratory results, and the percent of laboratories passing the WS proficiency test for benzo(a)pyrene within the acceptance limits. The acceptance limits were calculated to be plus or minus two standard deviations from the estimated mean recovery, as stipulated in CFR §141.24(h)(19)(i).

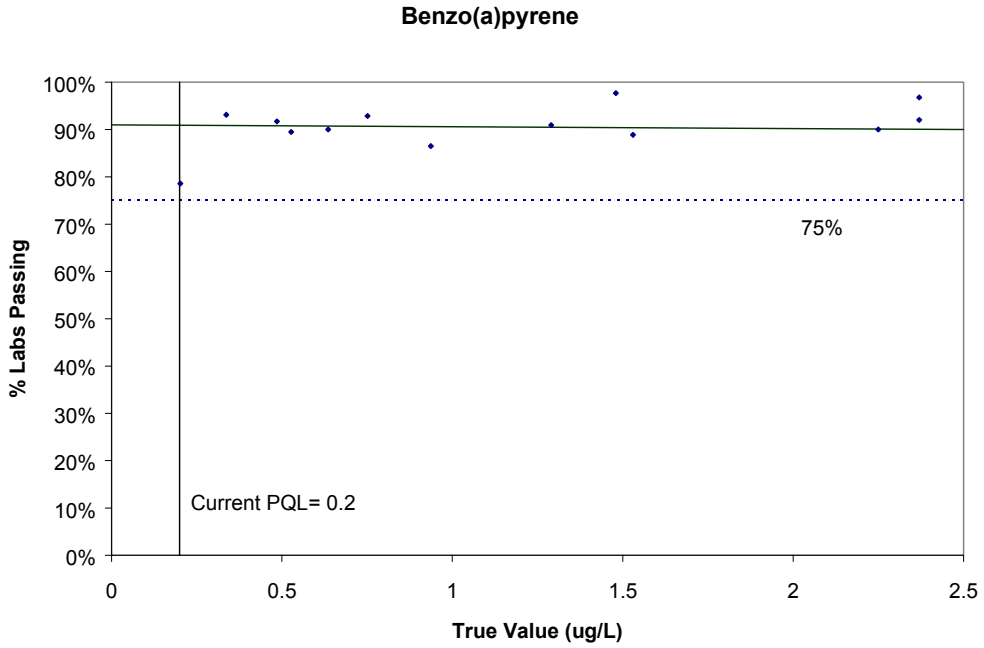
Table 7. Evaluation of PE Data for Benzo(a)pyrene from WS Studies Using 2 x S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True"Value (µg/L)	# Results from EPA and State Labs	% Labs Passing Acceptance Limits
31	0.202	14	79
32	0.337	29	93
30	0.485	12	67
38	0.53	38	84

WS #	Spiked "True"Value (µg/L)	# Results from EPA and State Labs	% Labs Passing Acceptance Limits
36	0.64	40	88
34	0.75	28	89
37	0.94	37	89
33	1.29	22	82
40	1.48	43	91
35	1.53	27	70
26	2.25	10	83
39	2.37	31	94
41	2.37	25	84
26	15.5	12	70

Figure 6 shows the plot of the benzo(a)pyrene data for WS 24 to 41, and the linear regression line. There is no meaningful relationship in these data, in large part because the true values of the samples are so high that a very large percentage of the labs passed all the PE series. Further, only one PE sample approached the current PQL (WS 31), and these results (79 percent passing) support the current PQL.

Figure 6. PQL Evaluation from PE WS Data: Benzo(a)pyrene



Conclusion for Benzo(a)pyrene

As noted in the method comparison, a more sensitive method (EPA 525.2) has been approved since the promulgation of benzo(a)pyrene, replacing an older and less sensitive version (EPA 525.1). The method usage evaluation shows that in recent years, a majority of EPA and State laboratories in the PE studies have chosen to use this more sensitive method out of all the approved methods for benzo(a)pyrene. The WS data do not afford a re-evaluation of the PQL, and at best, support the current value. There is no clear evidence to support a change from the current PQL of 0.2 µg/L. The current PQL appears to be appropriate.

Beryllium

Results of the Method Comparison

With the Phase V IOCs (57 FR 31776), EPA approved multiple analytical methods for determination of beryllium in drinking water, including an atomic absorption–furnace (AAF) method (EPA 210.2), an inductively coupled plasma atomic emission spectroscopy (ICP-AES) method (EPA Methods 200.7) and ICP-mass spectroscopy method (ICP-MS) (EPA 200.8). EPA 210.2 has since been removed from the approved list and replaced by four newer methods: EPA 200.9 (AA–platform); and three voluntary consensus standard methods, including Standard Methods 3113B (AA–furnace) and 3120B (ICP-AES) and ASTM Method D3645-93B (AA–furnace). These methods are listed in Table 8. The MDLs of EPA Methods 200.7 and 200.8 do not present any improved sensitivity capabilities. However, Method 200.9 is about five

times more sensitive than the most sensitive method approved at the time of promulgation (EPA 200.7).

Table 8. Results of the Analytical Methods Comparison for Beryllium (Newly Promulgated Methods Indicated in Bold)

MCL = 4 µg/L	Current PQL = 1 µg/L		DL▲ = 0.02-0.3 µg/L		Acceptance Limit† = ± 15%
Methods Approved At Promulgation			**Currently Approved Methods (141.23)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 200.7[1]	ICP-AES	0.1	EPA 200.7[2]	ICP	0.3
EPA 200.8[1]	ICP-MS	0.2	EPA 200.8[2]	ICP-MS	0.3
EPA 210.2[1]	AA; Furnace	0.2	**EPA 200.9[2]**	AA; Platform	0.02
			3113B[3]	AA; Furnace	N/A*
			3120B[3]	ICP	N/A*
			D3645-93B[4]	AA; Furnace	N/A*

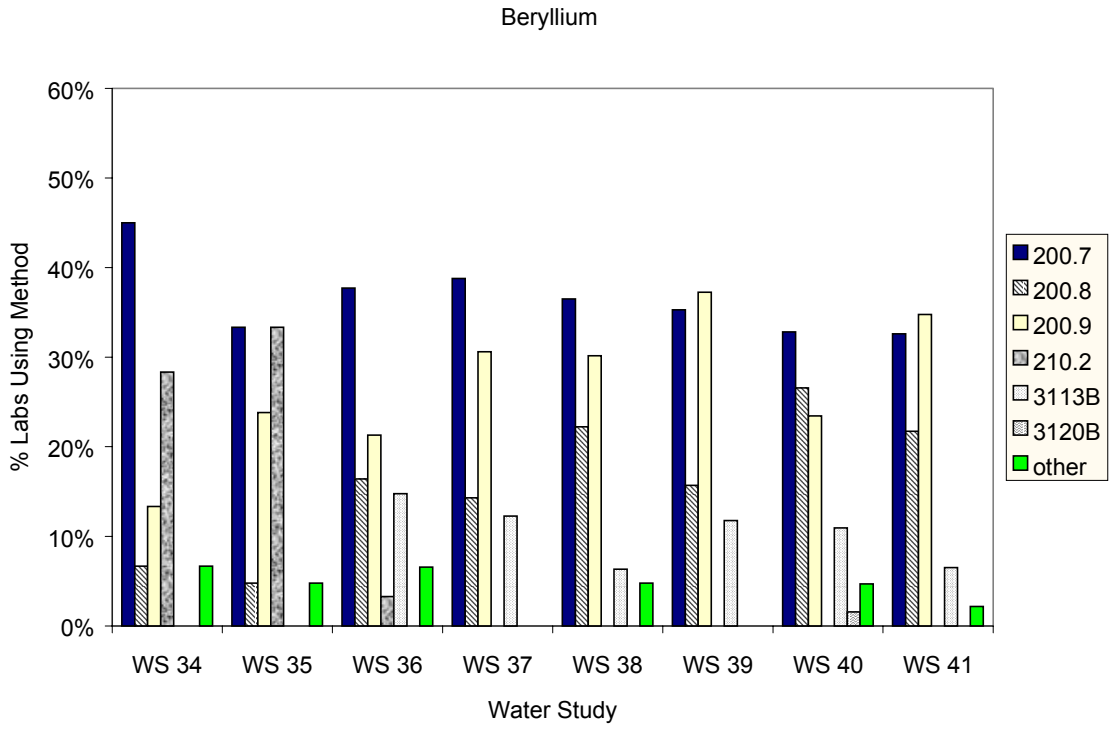
[1] "Methods for Chemical Analysis of Water and Wastes (MCAWW), EPA/600/4-79-020, March 1983.
[2] "Methods for the Determination of Metals in Environmental Samples Supplement I," EPA/600/R-94/111, May 1994.
[3] *Standard Methods for the Examination of Waste and Wastewater*. American Public Health Association, 1015 Fifteenth Street NW, Washington, DC 20005.
[4] *Annual Book of ASTM Standards*, Vol. 11.01. American Society for Testing and Materials, 1961 Race Street. Philadelphia, PA 19103.
▲ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.23(a)(4)(i). These values vary depending on analytical method.
*MDLs are not specified for non-EPA (i.e., voluntary consensus standard) methods.
† Acceptance limits are listed at 40 CFR §141.23(k)(3)(ii) for inorganic compounds.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the analytical techniques used by the EPA and State laboratories in WS studies 34 to 41 is shown in Figure 7. The category of "other" techniques include additional methods used by participating laboratories, as well as "unknown" methods, i.e., methods for which laboratories did not report any information on the type of method used. As shown in Figure 7, EPA Methods 200.7 and 210.2 were the most widely used methods in WS 34 and 35. By WS 37, laboratories ceased to use EPA 210.2 and relied more on EPA 200.9. From WS 37 to 41, EPA Methods 200.7, 200.8, and 200.9 were most commonly used. The two 3000-series Standard Methods were used to a far lesser extent than these EPA methods.

Figure 7. Distribution of Analytical Techniques by WS Study: Beryllium



b. Results of the PQL Analysis

The current PQL (1.0 µg/L) was originally determined using PE data from WS 24 through 27 (56 FR 60949). A PQL re-evaluation was attempted using more current data spanning WS 24 to 41. Table 9 summarizes the results of these water studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the beryllium results evaluated using an acceptance limit of ± 15 percent (as indicated at 40 CFR §141.23(k)(3)(ii)).

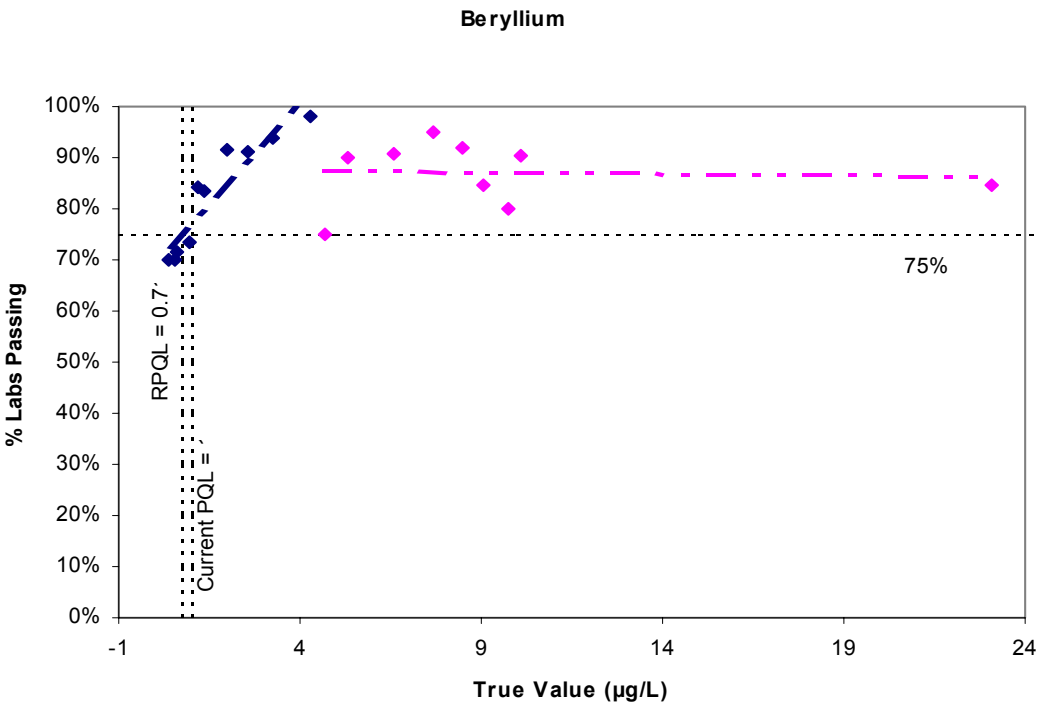
Table 9. Evaluation of Beryllium Data from WS Studies Using the 15% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 15% Acceptance Limits
25b	0.400	20	70.0
26a	0.530	40	70.0
24a	0.600	35	71.4
32	0.933	60	73.3

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 15% Acceptance Limits
39	1.20	51	84.3
35	1.33	42	83.3
25a	2.00	24	91.7
41	2.58	46	91.3
31	3.27	33	93.9
37	4.26	49	98.0
27	4.67	24	75.0
34	5.33	60	90.0
40	6.60	64	90.6
36	7.70	61	95.1
30	8.47	49	91.8
33	9.07	39	84.6
29	9.76	25	80.0
38	10.1	63	90.5
26b	23.1	46	84.8

The data in Table 9 seems to indicate that a linear relationship might exist between "true" value concentration and percentage of labs passing. Furthermore, a PQL re-evaluation appeared possible because the percentage of labs passing fell within the 75 percent criterion for some studies, and the true values from the water studies approximated the general range of the current PQL. Visual evaluation of the laboratory passing percentages around the current PQL of 1 µg/L indicate that this value is still appropriate and unlikely to change. The graph in Figure 8 illustrates this relationship between the spike concentrations and the laboratory passing rates. As shown in Figure 8, the recalculated PQL of 0.71 µg/L, is slightly lower than the current PQL.

Figure 8. Two-part Distribution of Beryllium WS Data:



Conclusion for Beryllium

The method comparison results indicate that EPA 200.9 is now the most sensitive method for determination of beryllium in drinking water and its MDL has improved by five-fold over the most sensitive MDLs achieved at the time of promulgation. EPA 200.7 was used more widely in previous years but is less sensitive. As revealed by the results of method usage over time, EPA 200.9 is the most commonly employed method for beryllium determination in recent PE studies. These trends seem to imply a shift in analytical capabilities for beryllium determination toward greater sensitivity. Thus, EPA and State laboratories are likely to reach lower detection limits today compared to the year of NPDWR promulgation. The re-evaluation of the PQL using a linear regression was calculated to be 0.71 µg/L, a value close to the current PQL of 1 µg/L. Although it may be possible to lower the PQL slightly based on more recent PE data, the current PQL is still appropriate.

Bis(2-ethylhexyl)phthalate

Results of the Method Comparison

At the time of the Phase V SOC promulgation (57 FR 31776), EPA Methods 506 and 525.1 were the only approved methods for the analysis of bis(2-ethylhexyl)phthalate (also known as di(2-ethylhexyl)phthalate). Since that time, EPA 506, which uses LLE or LSE GC with PID, has remained on the approved methods list while EPA 525.1, which utilizes LSE GC/MS, has been

replaced by a more sensitive version, EPA 525.2. This increased sensitivity, however, is only marginal, as evidenced by the similarity of their MDLs. Table 10 lists the approved methods, techniques, and MDLs, during and after the time of rule promulgation.

Table 10. Results of the Analytical Methods Comparison for Bis(2-ethylhexyl)phthalate (New Methods in Bold)

MCL = 6 µg/L Current PQL = 6 µg/L DL▲ = 0.6 µg/L Acceptance Limit† = ± 2 x S.D.					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 525.1[1]	LSE, GC/MS	0.6 - 0.8*	**EPA 525.2[3]**	LSE, GC/MS	0.46 - 7.9*
EPA 506[2]	LLE or LSE, GC w/ PID	2.25	EPA 506[3]	LLE or LSE, GC w/ PID	2.25

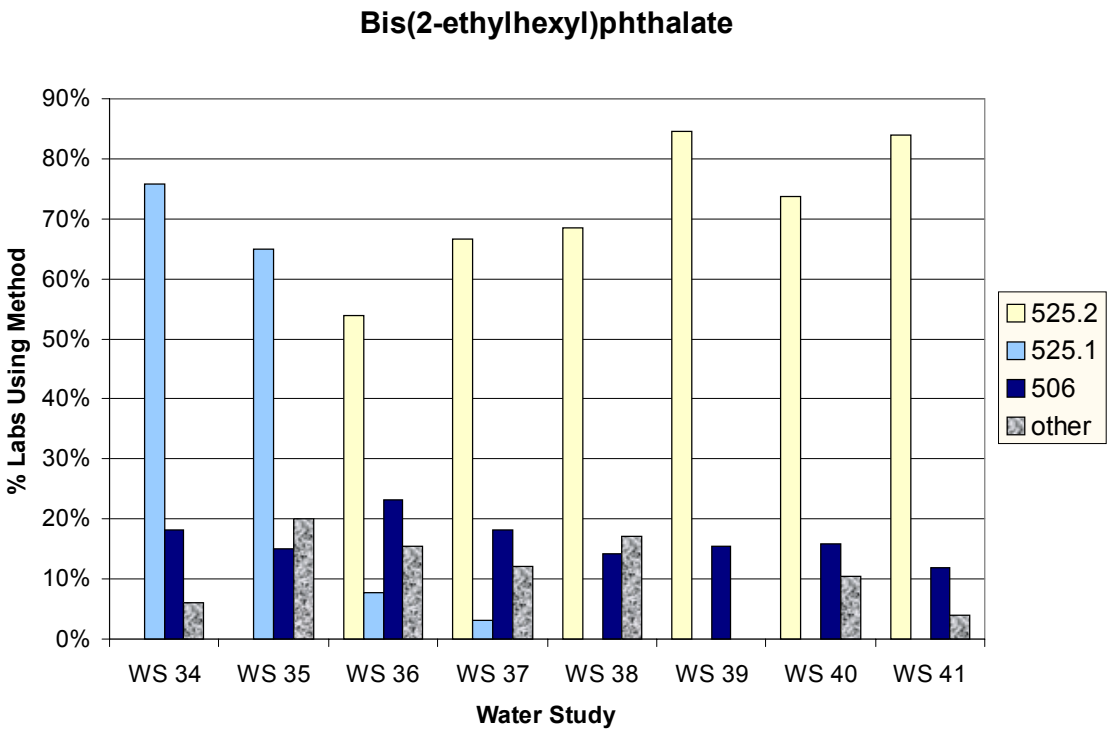
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water, Supplement I," EPA/600/4-90/020, July 1990.
[3] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation, and/or laboratory/analyst performance.
▲ Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18)
† Acceptance limits for organic compounds are listed at 40 CFR 141.24(h)(19)(i)

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the analytical methods used during WS 34 to 41 by participating EPA and State laboratories are illustrated in Figure 9. The category of "other" represents any alternative or unreported methods. As shown in Table 10, use of EPA 525.1 decreased significantly, corresponding to the introduction of EPA 525.2 during WS 36. By WS 38, EPA 525.1 was no longer used by any laboratories for analyzing bis(2-ethylhexyl)phthalate. Laboratories overwhelmingly chose to use the LSE GC/MS technique (either EPA 525.1 or its replacement, EPA 525.2) over EPA 506, which utilized the LLE or LSE GC with PID.

Figure 9. Distribution of Analytical Techniques by WS Study: Bis(2-ethylhexyl)phthalate



b. Results of the PQL Analysis

PE data from WS 24 to 41 were compiled to re-evaluate the PQL. Table 11 shows the WS number, the true value concentration, the number of participating laboratories, and the percent of laboratories passing within acceptance limits. These limits were calculated to be two times the standard deviation, as stipulated in 40 CFR §141.24(h)(19)(i). Note that data were unavailable for WS 25 and 28.

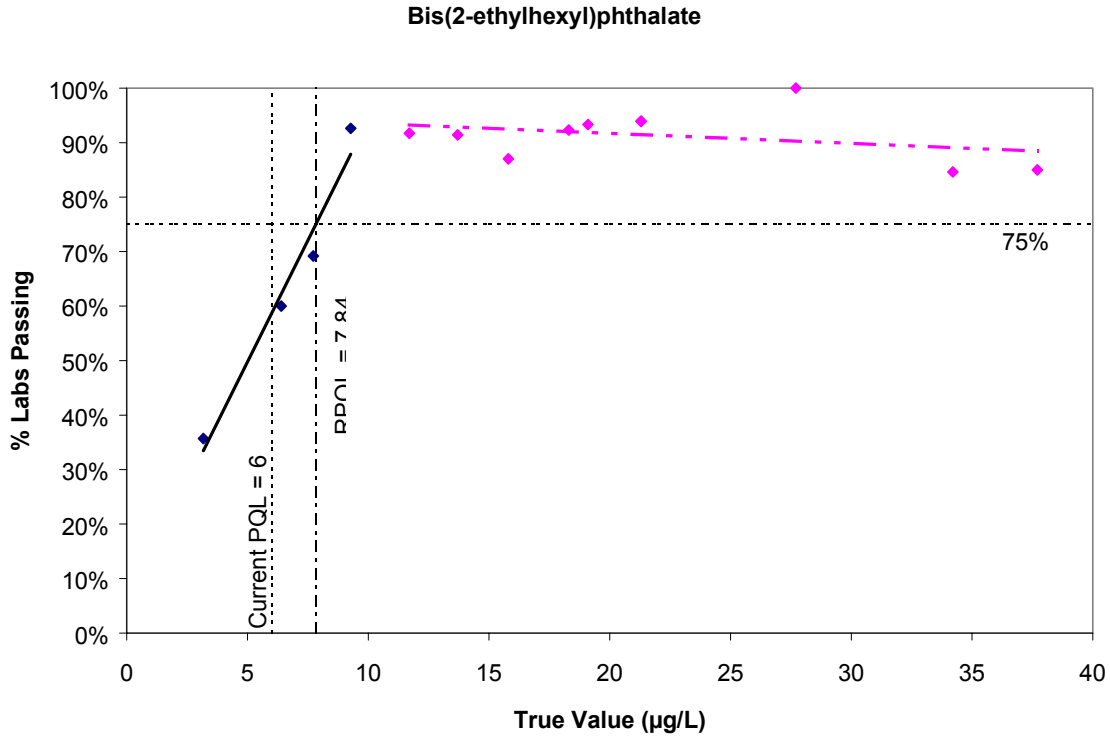
Table 11. Evaluation of Bis(2-ethylhexyl)phthalate Data from WS Studies Using 2 x S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ±2 x S.D. Acceptance Limits
24a	3.18	14	35.7
29	4.58	8	75
30	6.40	15	60
26b	7.73	13	69.2

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ±2 x S.D. Acceptance Limits
32	9.28	27	92.6
31	11.7	12	91.7
38	13.7	35	91.4
41	15.3	25	84
33	15.8	23	87
27	17.3	7	85.7
36	18.3	39	92.3
24b	19.1	15	93.3
37	21.3	33	93.9
34	21.3	33	93.9
39	27.7	26	100
40	32.4	38	89.5
26a	34.2	13	84.6
35	37.7	20	85

Using the data in Table 11, a linear regression was performed by plotting the percentage of the laboratories passing for WS 24 to 41 (excluding WS 25 and 28) against the spiked value of bis(2-ethylhexyl)phthalate (Figure 10). Simple visual examination of the graph shows that the percentage of laboratories achieving acceptable results approximates 75 percent at a concentration of 7.84 µg/L. This concentration is higher than the current PQL of 6.0 µg/L, which was originally estimated using PE data from WS 23, 24, and 27 (57 FR 60953).

Figure 10. Two-part Distribution of Bis(2-ethylhexyl)phthalate WS Data



Conclusion for Bis(2-ethylhexyl)phthalate

Since the time of the Phase V SOC rule promulgation, EPA 525.2 has replaced EPA 525.1. This new method provides a marginally greater degree of sensitivity. The EPA and State laboratories have overwhelmingly chosen to use EPA 525.2 over any other available methods as evidenced by the plot of method usage over time. The re-evaluation of the PQL using a linear regression calculated from WS 24a, 26b, 30 and 32 data showed that a new PQL could be derived. The re-evaluated PQL of 7.84 µg/L is higher than the original PQL of 6 µg/L (57 FR 31802).

Cadmium

Results of the Method Comparison

The 1991 NPDWRs for Phase II IOCs listed Atomic Absorption–Furnace (AAF; EPA 213.2) and Inductively Coupled Plasma (ICP; EPA 200.7A) as approved analytical methods for the determination of cadmium in drinking water (57 FR 31776). Since the promulgation of the rule, these methods have been replaced by four new or updated methods; three EPA methods (EPA Methods 200.7, 200.8, and 200.9), and one voluntary consensus standard method (Standard Method 3113B). Table 12 compares the detection limits of approved methods during and after promulgation of the NPDWR for cadmium and shows EPA 200.9 to be the most sensitive

method for detecting cadmium in drinking water compared to all other original and current methods.

Table 12. Results of the Analytical Methods Comparison for Cadmium (Newly Promulgated Methods Indicated in Bold)

MCL = 5 µg/L	Current PQL = 2 µg/L		DL▲ = 0.1-1.0 µg/L		Acceptance Limit† = ± 20%
Methods Approved At Promulgation			**Currently Approved Methods (141.23)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 200.7A[1]	ICP-AES	1	**EPA 200.7[2]**	ICP-AES	1.0
EPA 213.2[1]	AAF	0.1	**EPA 200.8[2]**	ICP-MS	0.5
			EPA 200.9[2]	AA; Platform	0.05
			SM 3113B[3]	AA; Furnace	N/A◇

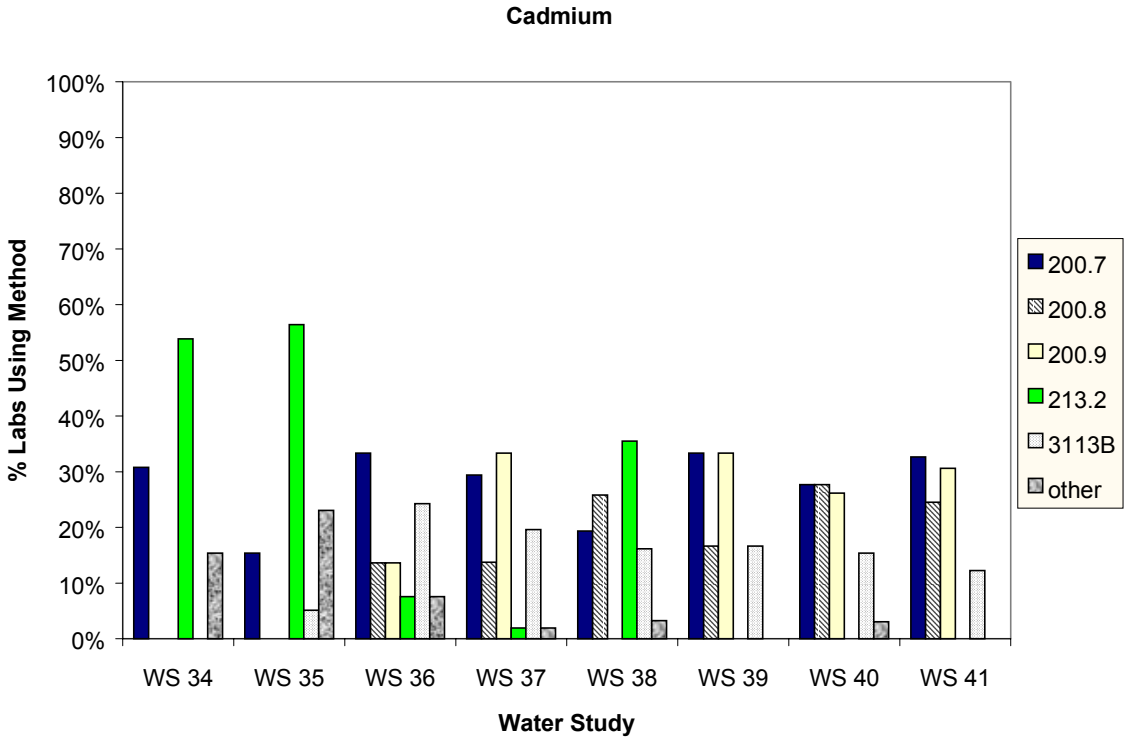
[1] "Methods for Chemical Analysis of Water and Wastes (MCAWW)," EPA/600/4-79-020, March 1983.
[2] "Methods for the Determination of Metals in Environmental Samples--Supplement I," EPA/600/R-94/111, May 1994.
[3] 18th and 19th editions of *Standard Methods for the Examination of Water and Wastewater*, 1992 and 1995. American Public Health Association.
▲ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.23(a)(4)(i) and depend on analytical method.
† Acceptance limits are listed at 40 CFR §141.23(k)(3)(ii).
◇ MDLs for non-EPA methods are not specified.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 11 shows the distribution of analytical techniques used by EPA and State laboratories for WS studies 34 to 41. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as "unknown" methods, i.e., methods for which laboratories did not report any information on the type of method used. During WS 34 and 35, EPA 213.2 was the most widely used method for determining cadmium in drinking water. By WS 36, its use was considerably diminished, but a resurgence was seen in WS 38, only to be phased out in WS 39. Subsequently, EPA Methods 200.7, 200.8, and 200.9 were all used with relatively the same frequency by the participating laboratories in the PE studies. Use of SM 3113B lessened over the period between WS 36 and 41.

Figure 11. Distribution of Analytical Techniques by WS Study: Cadmium



b. Results of the PQL Analysis

The current PQL of 2.0 µg/L was originally set using PE data from WS 22 through 25 (56 FR 3549). With the availability of more current data from WS 24 to 41, a PQL re-evaluation was attempted. Table 13 summarizes the results of these water studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the cadmium results evaluated using an acceptance limit of ± 20 percent, as designated in 40 CFR § 141.23(k)(3)(ii).

Table 13. Evaluation of Cadmium Data from WS Studies Using the 20% Acceptance Limits (In Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits
38	2.12	62	85.5
35	2.80	39	87.2
29	2.80	34	88.2

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits
32	4.80	67	97.4
40	6.31	65	87.7
26b	9.20	62	91.9
37	10.2	51	98.0
24b	10.4	61	95.1
31	12.8	35	91.4
24a	15.4	61	90.2
41	18.2	45	95.6
34	23.0	65	96.9
25	27.6	40	100
39	28.5	54	98.1
27	29.3	40	92.5
36	34.0	66	98.5
30	39.0	66	98.5
33	49.0	38	97.4
26a	53.9	62	96.8

The data in Table 13 were not adequate to perform a PQL re-evaluation. EPA's preferred format for evaluating a PQL is to develop a regression (or graphical analysis) using the true value concentration and the percentage of laboratories passing the performance evaluation. The PQL is then set at a concentration in which 75 percent of those laboratories pass. In this instance, however, the participating laboratories passed the evaluation at an average rate of 93 percent, well above the 75 percent criterion. Also, all of the spiked "true" values were well above the original PQL of 2 µg/L.

Conclusion for Cadmium

A comparison of the analytical methods approved during and after the promulgation of the NPDWR for cadmium show that the four current methods have sensitivities similar to, or slightly better than, those of the original methods, with EPA 200.9 being the most sensitive (with an MDL of 0.05 µg/L). Laboratories that participated in the PE water studies chose to utilize EPA 213.2 in the WS studies prior to WS 38 but then chose to utilize EPA Methods 200.7, 200.8, and 200.9 with similar frequency. Review and analysis of the PE data did not result in the estimation of a new PQL because all of the EPA and State laboratories in the WS studies evaluated surpassed the required 75 percent criterion typically used to determine a new PQL. In addition,

all of the WS spike concentrations were above the current PQL of 2 µg/L. However, laboratory passing rates of greater than 85 percent at concentrations slightly above the current PQL suggest that the PQL could be lower.

Carbofuran

Results of the Method Comparison

At the promulgation of the NPDWRs for synthetic organic chemicals (56 FR 3552), one analytical method (EPA 531.1) was approved for determination of carbofuran in drinking water. Since that time, the sensitivity of EPA 531.1 has improved, as indicated by a lower MDL. One additional method, Standard Method (SM) 6610, has been included as an approved method for carbofuran analysis. Both current methods use the HPLC technique and have similar MDLs. Table 14 summarizes the approved methods, both past and present, for determination of carbofuran.

Table 14. Results of the Analytical Methods Comparison for Carbofuran (Newly Promulgated Methods in Bold)

MCL = 40 µg/L	**Current PQL = 7 µg/L**		**DL‸ = 0.9 µg/L**	**Acceptance Limit† = ± 45%**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 531.1[1]	HPLC	0.9	EPA 531.1[2]	HPLC	0.52
			SM 6610[3]	HPLC	0.53

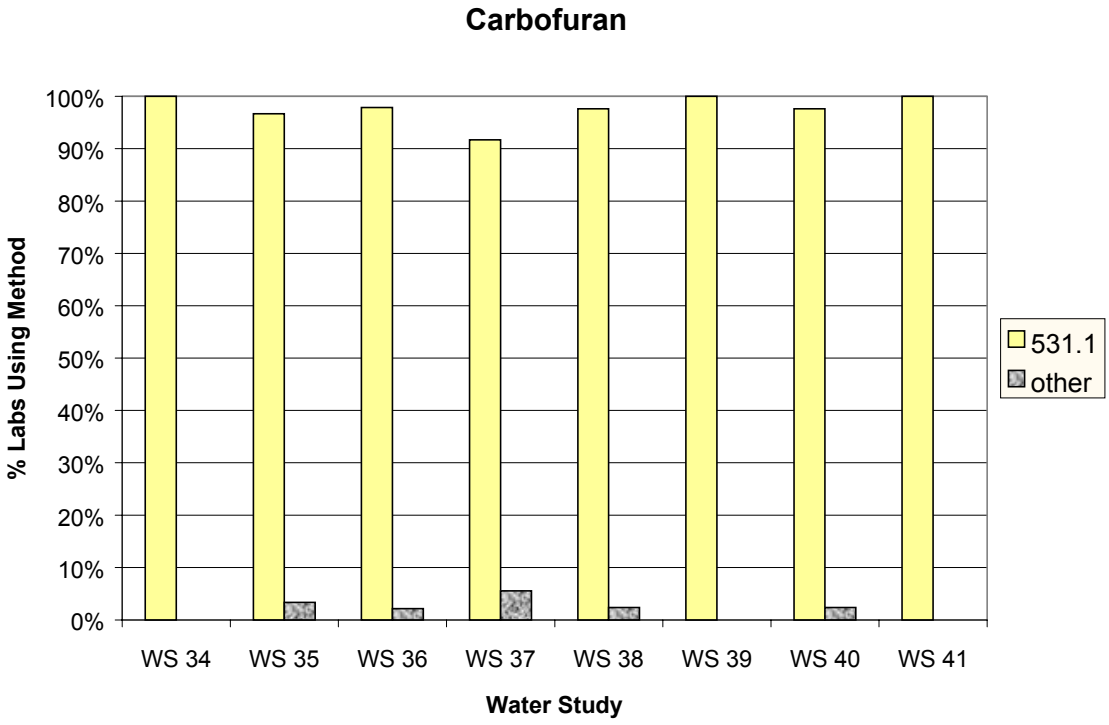
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
[3] "Supplement to the 18th edition of Standard Methods for the Examination of Water and Wastewater," 1994.
‸ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(h)(18).
† Acceptance limits for organic compounds are listed at 40 CFR § 141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 12 illustrates the methods chosen by EPA and State laboratories for carbofuran analysis during WS PE studies 34 to 41. The category of "other" includes any unidentified or unreported techniques used by participating laboratories. As shown in Figure 12, the predominant method used by laboratories participating in the WS studies is EPA 531.1. The smallest percentage of labs using this method is 91.7 percent (in WS 37), indicating wide usage compared to SM 6610 or any other available methods.

Figure 12. Distribution of Analytical Techniques by WS Study: Carbofuran



b. Results of the PQL Analysis

The current PQL of 7 µg/L was derived from multiplying the interlaboratory method detection limit (IMDL) of 0.7 µg/L by a factor of ten (54 FR 22062). To conduct a PQL re-evaluation, the numerical data from WS 24 to 41 were analyzed (though no data were available for WS 28). Table 15 summarizes each WS result including the spiked (or "true") value, the number of participating laboratories, and the percentage of laboratories passing within the specified acceptance limit for carbofuran (± 45 percent of the spiked value, as specified in 40 CFR §141.24(h)(19)(i)).

Table 15. Evaluation of Carbofuran Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
29	4.00	10	100
30	5.78	26	92
32	7.67	36	94
31	11.3	14	86

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
24a	15.6	11	100
26b	17.5	13	92
34	18.5	43	91
27	20.7	8	88
25a	24.2	5	80
33	24.8	33	94
38	33.6	42	95
26a	36.3	13	100
36	37.8	47	98
35	42.8	60	92
41	43.7	29	97
24b	44.5	11	100
25b	48.3	5	100
37	48.9	36	97
40	55.0	42	100
39	74.5	31	97

Re-evaluation of the PQL by a linear regression approach was not feasible using the data shown in Table 15. The percentage of laboratories passing within the acceptance limit was well above the 75 percent criterion historically used to calculate the PQL. Also, very few (e.g., only WS 29, 30, and 32) of the above WS studies provided a sample with a true value concentration near the original PQL. Because of these data limitations, the PQL could not be re-evaluated using the historical linear regression approach. Instead, at concentrations approaching nearly half of the current PQL, laboratories in WS 29 were observed to achieve a 100 percent passing rate, implying strong analytical capabilities at a low concentration. This observation could have implications for lowering the PQL.

Conclusion for Carbofuran

Since the time of promulgation of the original methods, one new method (SM 6610) has been added for carbofuran analysis. The current EPA 531.1 is nearly twice as sensitive as the previous version, and the plot of method usage over time illustrates that EPA 531.1 was the most commonly used method for the determination of carbofuran. Together, these facts imply that analytical methods capabilities have improved over time. The PE data from WS studies 24 to 41, however, were not useful for a PQL re-evaluation because of the extremely high number of

laboratories passing within the accepted limit for carbofuran. While the high success rate of laboratories at some low concentrations may present a potential argument for lowering the PQL from 7 µg/L, there are no data available to support changing the original PQL.

Carbon Tetrachloride

Results of the Method Comparison

In July 1987, the final NPDWR for eight Phase I VOCs approved the use of EPA Methods 502.1, 502.2, 524.1, and 524.2 for the determination of carbon tetrachloride in drinking water (52 FR 25690). The current approved methods for carbon tetrachloride determination are EPA Methods 502.2, 524.2, and 551.1. Table 16 summarizes the MDLs for both the original and currently approved versions of the methods. As shown in Table 16, the three new methods have greater detection sensitivity than EPA 524.1 but not when compared to EPA 502.1.

Table 16. Results of the Analytical Methods Comparison for Carbon Tetrachloride (New Methods in Bold)

MCL = 5 µg/L	**Current PQL = 5 µg/L**	**DL▲ = 0.5 µg/L**	**Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)**		
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL ◊ (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.003	**EPA 502.2[2]**	Purge and Trap GC	0.01 - 0.02
EPA 502.2[1]	Purge and Trap GC	0.01	**EPA 524.2[2]**	GC/MS	0.08 - 0.21
EPA 524.1[1]	GC/MS	0.3	**EPA 551.1[2]**	LLE/GC with ECD	0.006 - 0.05
EPA 524.2[1]	GC/MS	0.21			

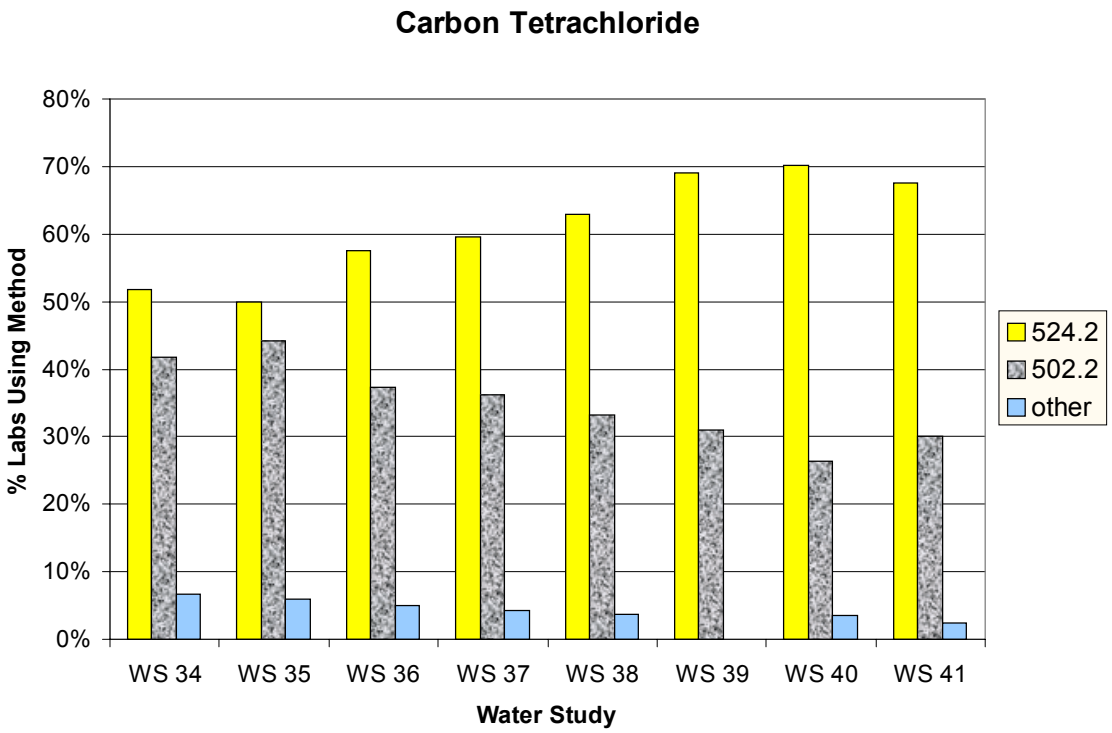
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for VOCs are listed at 40 CFR § 141.24(f)(17)
† Acceptance limits are listed at 40 CFR § 141.24(f)(17)(i)

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the different methods used by the EPA and State laboratories during WS studies 34 to 41 are shown in Figure 13. The category of "other" contains those methods that were unknown or unidentified by the participating laboratories. As shown in Figure 13, EPA Methods 524.2 and 502.2 are currently the preferred methods used by laboratories for determination of carbon tetrachloride. Use of the original methods, EPA Methods 502.1 and 524.1, was not apparent over this time period; plotting data from studies prior to WS 34 might reveal more information on the use of these methods.

Figure 13. Distribution of Analytical Techniques by WS Study: Carbon Tetrachloride



b. Results of the PQL Analysis

The original PQL of 5 µg/L (52 FR 25700) for carbon tetrachloride was determined from PE data from WS 8 to 11. Re-evaluation of the PQL was attempted using data from WS studies 24 through 41. Table 17 summarizes the results of these WS studies providing the study number, the spiked value for the WS sample, the number of participating laboratories, and the percent of laboratories passing the WS proficiency test for carbon tetrachloride within the specified acceptance limits for carbon tetrachloride (± 20 percent for a true value greater than10 µg/L, or ± 40 percent for a true value lower than 10 µg/L as specified at 141.24(f)(17)(i)).

Table 17. Evaluation of Carbon Tetrachloride Data from WS Studies Using Either 20% or 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
24	4.56	56		96
34	6.27	60		100
30	6.46	59		98
27	8.48	37		97
31	8.69	36		100
40	8.90	57		98
25	9.18	37		95
29	10.4	36	81	
35	10.8	34	88	
36	12.6	59	97	
37	12.7	47	87	
33	13.4	34	88	
41	14.2	40	100	
32	14.5	55	89	
38	15.6	54	94	
26	16.7	59	85	
39	19.2	42	83	

From Table 17, it can be concluded that the available PE data for carbon tetrachloride are insufficient for a PQL re-evaluation. For the WS studies evaluated, the participating labs passed the proficiency exams at a passing rates greater than the standard 75 percent acceptance criterion used to determine the PQL. In addition, only one WS study (WS 24) had a concentration lower than the current PQL. However, passing rates of greater than 96 percent at concentrations close to the current PQL suggest that the current PQL of 5 µg/L could be possibly be lower.

Conclusion for Carbon Tetrachloride

The method comparison results show that since the promulgation of analytical methods under the NPDWR, three new methods (EPA Methods 502.2, 524.2, and 551.1) have replaced the two original analytical methods (EPA Methods 502.1 and 524.1). While EPA 551.1 is the most sensitive of the three currently approved methods, this method is not currently used by EPA or State laboratories according to the available WS data. Instead, EPA 524.2, the least sensitive of

the three current methods, has been the primary method of choice. The MDL of EPA 524.2 represents a mixed change in analytical methods, as it is more sensitive than EPA 524.1 but less sensitive than EPA 502.1. Evaluation of the quantitative PE data showed that the majority of the laboratories conducting WS analyses surpassed the 75 percent criterion. Because of the high percentage of laboratories passing and a lack of spike samples at concentrations below the current PQL, a re-evaluation of the PQL could not be performed using this approach. However, high passing rates at values close to the current PQL of 5 µg/L suggest that a lower PQL is possible.

Chlordane

Results of the Method Comparison

With the 1991 promulgation of the Phase II Rule for SOCs, three analytical methods were approved for the determination of chlordane in drinking water: EPA Methods 505 (GC/microextraction), 508 (GC/ECD), and 525.1 (LSE/GC/MS) (56 FR 3526). Since the promulgation of this rule, EPA 525.1 was removed and EPA Methods 525.2 (LSE, GC/MS) and 508.1 (GC/LSE/ECD) were added to the approved list. Table 18 lists detection limits for these methods. Using the highest value of the range of MDLs reported, EPA Methods 508 and 508.1 are both approximately 30 times more sensitive than EPA 505.

Table 18. Results of the Analytical Methods Comparison for Chlordane (Newly Promulgated Methods are Indicated in Bold)

MCL = 2 µg/L	**Current PQL = 2 µg/L**		**DL▲ = 0.2 µg/L**	**Acceptance Limit† = ± 45%**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	GC, microextraction	0.14	EPA 505[2]	GC, microextraction	0.14
EPA 508[1]	GC with ECD	0.0015	EPA 508[2]	GC, ECD	0.00041 - 0.0041*
EPA 525.1[1]	LSE, GC/MS	2	**EPA 508.1[2]**	LSE, GC with ECD	0.001 - 0.004*
			EPA 525.2[2]	LSE, GC/MS	0.065 - 0.17*

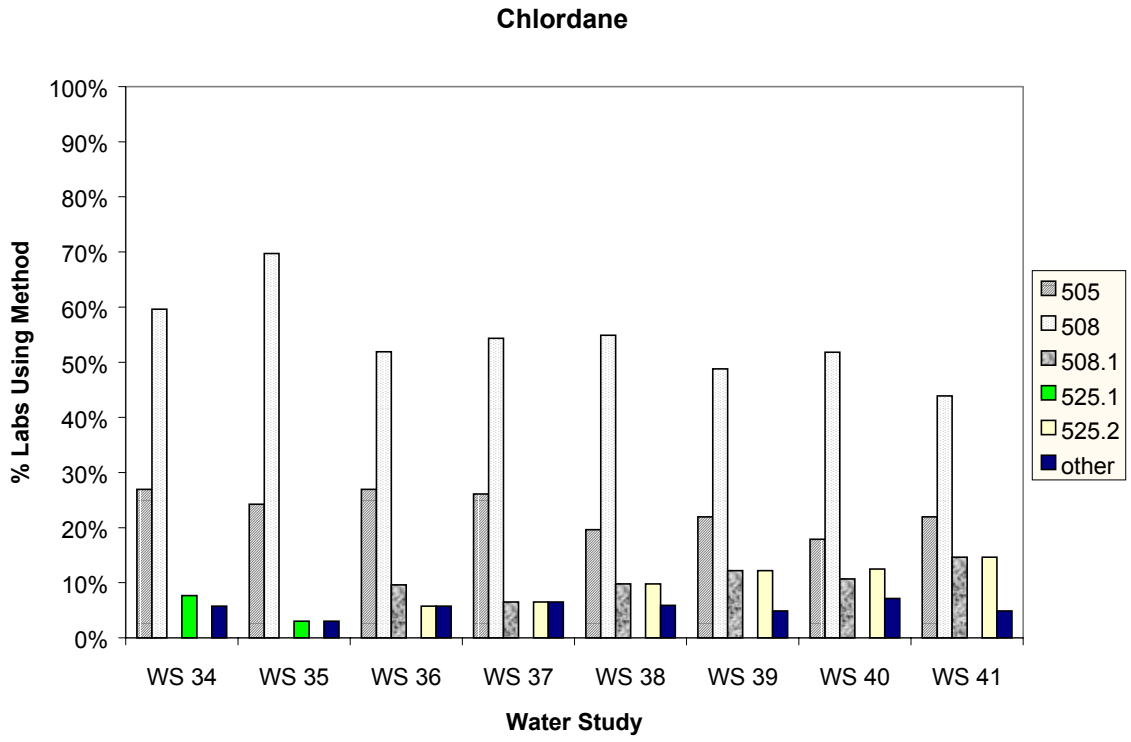
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).
† Acceptance limits for organic compounds are listed at 40 CFR §141.24(h)(19)(i).
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 14 plots the distribution of analytical techniques used by EPA and State laboratories in WS 34 to 41. The "other" techniques represent methods which were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 14, the majority of laboratories used EPA Method 508 for determination of chlordane in WS 34 to 41. EPA 525.1, which was used quite minimally in earlier WS studies, was replaced by EPA 525.2 during WS 36. Laboratories also began to employ EPA Methods 508.1 during WS 36. For WS 34 to 41, EPA 505 consistently remained the second-most commonly used method after EPA 508.

Figure 14. Distribution of Analytical Techniques by WS Study: Chlordane



b. Results of the PQL Analysis

The Agency derived the current chlordane PQL of 2 µg/L by multiplying the detection limit by a factor of ten (56 FR 3552). With the availability of recent PE WS data, efforts were made to reassess the PQL using PE data from WS 24 to 41. Table 19 summarizes the data from these WS studies, indicating the study number, the spiked or "true" value of the WS sample, the number of results from EPA and State laboratories, and the calculated percentage of laboratories whose results successfully passed within federally designated acceptance limits for chlordane. These acceptance limits are specified in 40 CFR §141.24(h)(19)(i) to be ± 45 percent.

Table 19. Evaluation of Chlordane Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
29	0.833	25	88.0
24a	1.32	40	87.5
27	1.84	28	96.4
26a	2.70	39	94.9
33	2.76	36	88.9
41	2.90	41	95.1
25a	3.30	22	95.5
39	3.57	41	95.1
30	4.20	49	93.9
37	4.44	46	93.5
24b	4.86	40	85.0
31	5.16	30	83.3
32	5.33	56	83.9
34	7.26	52	90.4
38	8.20	51	98.0
26b	9.60	39	97.4
40	11.8	56	94.6
25b	12.6	22	100
35	13.6	33	93.9
36	16.7	52	94.2

Table 19 shows that EPA and State laboratories consistently demonstrated high success rates, surpassing the 75 percent criterion for all evaluated water studies. Therefore, a new PQL could not be re-evaluated using this approach. Even at low spiked concentrations, including three samples below the current PQL, well over 80 percent of participating laboratories successfully determined results within the acceptance limits. This observation suggests the possibility that laboratories may be capable of determining chlordane at levels below the current PQL.

Conclusion for Chlordane

The plot of method usage over time (from WS studies) indicates consistent use of EPA Methods 508 and 505 over the duration of the selected studies, with laboratories favoring usage of EPA 508. EPA 508 represents the most sensitive currently approved method (Table 18). It appears that analytical capabilities for chlordane overall have improved since the time of NPDWR promulgation. The available numerical WS data do not support a reassessment of the PQL based on the 75 percent criterion, however, because the passing rates of laboratories always exceeded this value. Because such high passing rates were observed for some low spiked concentrations (e.g., 88 percent laboratory success for a concentration 2.5 times lower than the current PQL), it is possible that a lowered PQL might be appropriate. However, the desired quantitative reassessment of the PQL could not be performed using the historical approach.

Chromium

Results of the Method Comparison

In 1991, the Phase II rule for IOCs listed EPA Methods 218.2 (AAF) and 200.7 (ICP-AES) as the approved methods for determination of chromium in drinking water (57 FR 31776). Since that time, EPA 218.2 has been removed from the list of approved methods and four new methods have been added: two EPA Methods (200.8, ICP/MS; and 200.9, AA/Platform); and two Standard Methods (3113B, AA/Furnace; and 3120B, ICP). The sensitivity of the continuing method, EPA 200.7, appears to have remained similar over time, while the newer method (EPA 200.9) exhibits approximately ten times the sensitivity of the prior methods. EPA 200.8 is comparable in sensitivity to the old EPA 218.2. The detection limits of the Standard Methods are not specified. Table 20 summarizes the MDL information for all current and former approved methods.

Table 20. Results of the Analytical Methods Comparison for Chromium (Newly Promulgated Methods in Bold)

MCL = 100 µg/L	Current PQL = 10 µg/L		DL▲ = 1 - 7 µg/L	Acceptance Limit† = ± 15%	
Methods Approved At Promulgation			**Currently Approved Methods (141.23)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 200.7A[1]	Inductively Coupled Plasma	1.0 - 7.0*	EPA 200.7[3]	Inductively Coupled Plasma	4.0
EPA 218.2[2]	AA; Furnace	1.0	**EPA 200.8**[3]	ICP-MS	0.9
			EPA 200.9[3]	AA; Platform	0.1
			SM 3113B[4]	AA; Furnace	N/A◊
			SM 3120B[4]	Inductively Coupled Plasma	N/A◊

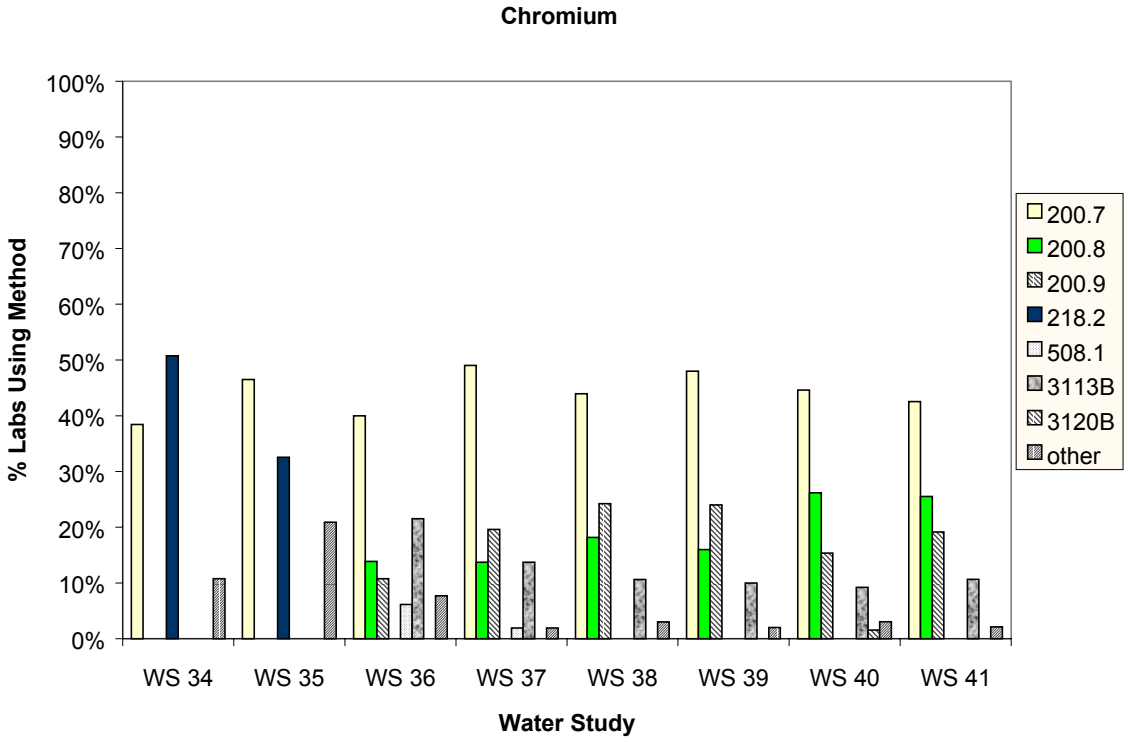
[1] "Inductively-Coupled Plasma Atomic Emission Analysis of Drinking Water," Appendix to Method 200.7, March 1987, U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.
[2] "Methods for Chemical Analysis of Water and Wastes (MCAWW)," EPA/600/4-79-020, March 1983.
[3] "Methods for the Determination of Metals in Environmental Samples Supplement I," EPA/600/R-94/111, May 1994.
[4] Standard Methods for the Examination of Water and Wastewater. American Public Health Association, 1015 Fifteenth Street NW, Washington, DC 20005.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation, and/or laboratory/analyst performance.
▲ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.23(a)(4)(i). The value may vary depending on analytical technique.
† Acceptance limits are listed at 40 CFR §141.23(k)(3)(ii) for inorganic compounds.
◊ N/A = not available. MDLs are not specified for non-EPA methods.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of analytical methods used by participating laboratories from WS 34 to 41 is shown in Figure 15. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as "unknown" methods, i.e., methods for which laboratories did not report any information on the type of method used. During WS 34 and 35, EPA Methods 200.7 and 218.2 were the most widely used among laboratories participating in the PE studies. By WS 36, EPA 218.2 was no longer in use. Overall, EPA 200.7 remained the most commonly used method during WS 34-41. Voluntary consensus standard methods SM 3120 and SM 3113B were also used in many WS studies.

Figure 15. Distribution of Analytical Techniques by WS Study: Chromium



b. Results of the PQL Analysis

The current PQL of 10 µg/L was derived using earlier PE data from WS 24 through 27 (56 FR 3549). For the PQL re-evaluation, data were taken from a broader range of studies, including more recent PE data (WS 24 to 41). The results of these water studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the reported results evaluated using an acceptance limit of ± 15 percent (§141.23(k)(3)(ii)) are summarized in Table 21.

Table 21. Evaluation of Chromium Data from WS Studies Using the 15% Acceptance Limits (In Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 15% Acceptance Limits
34	11.6	65	93.8
25a	15.0	41	92.7
39	23.9	50	94.0
24b	25.5	62	90.3
36	37.8	65	95.4
26a	50.2	64	95.3
41	55.5	47	100
25b	60.0	42	95.2
32	68.1	67	95.5
37	72.9	51	98.0
27	75.3	35	94.3
31	81.6	38	92.1
40	90.9	65	96.9
26b	94.6	64	93.8
29	110	33	87.9
35	119	43	90.7
24a	127	62	88.7
38	148	66	95.5
33	159	35	91.4
30	200	66	93.9

A re-evaluation of the PQL could not be performed using the available PE data in Table 21. To conduct a graphical PQL analysis requires laboratory success rates ranging below the 75 percent criterion, which participating laboratories consistently surpassed (achieving a passing rate of greater than 87 percent for all the WS studies evaluated). Furthermore, the spiked concentrations used in each water study were above the original PQL (10 µg/L).

Conclusion for Chromium

The method comparison results indicate that some methods approved after the promulgation of the Phase II Rule are more sensitive than the original methods (one of which was discontinued). Currently the most sensitive method is EPA 200.9 (AA–furnace). However, according to the plot of method usage over time, EPA 200.7 (ICP-AES) consistently has remained the most frequent choice for EPA and State laboratories, and the MDL of this method has not changed significantly. These facts suggest no significant alteration to the analytical capabilities of laboratories. Using the designated ± 15 percent acceptance limit, the evaluation of recent WS data revealed that these data are outside a range that would allow for a re-evaluation of the PQL. Thus, the PE data continue to support the existing PQL of 10 µg/L.

1,2-Dibromo-3-chloropropane (DBCP)

Results of the Method Comparison

The NPDWR for DBCP, a Phase II SOC, listed EPA 504 (GC with microextraction) as the only approved method for determination of this compound (56 FR 3526). Since then, EPA has replaced this method with an updated GC-microextraction method, EPA 504.1, and added a new technology, LLE/GC with ECD (EPA 551.1). Table 22 summarizes the approved methods at promulgation and currently approved methods. EPA 504.1 has an MDL roughly equal to the lowest MDL of the original EPA 504, and the MDL of the other new method, EPA 551.1, is less sensitive.

Table 22. Results of the Analytical Methods Comparison for DBCP (Newly Promulgated Methods are Indicated in Bold)

MCL = 0.2 µg/L	**Current PQL = 0.2 µg/L**		**DL▲ = 0.02 µg/L**	**Acceptance Limit† = ± 40%**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL* (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 504[1]	Microextraction, GC	0.01 - 0.2	**EPA 504.1[2]**	Microextraction, GC	0.01
			EPA 551.1[2]	LLE/GC with ECD	0.14 - 0.5*

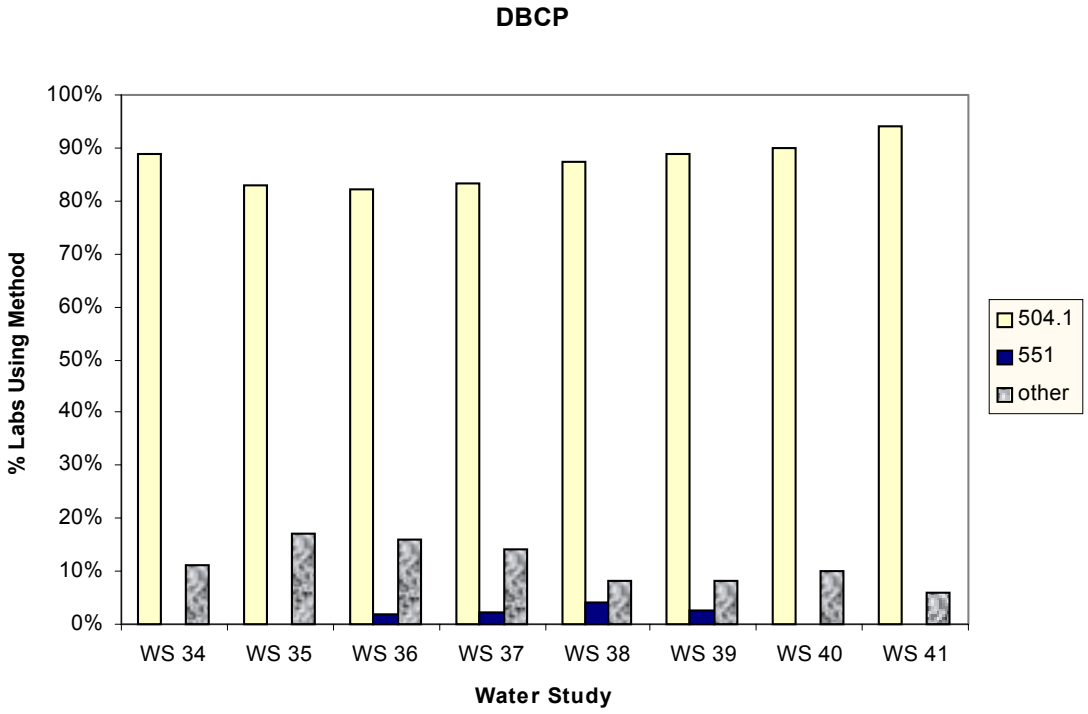
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).
† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 16 is a plot of the distribution of analytical techniques used by EPA and State laboratories in WS 34 to 41. The "other" techniques represent methods that were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 16, the majority of laboratories used EPA 504.1 during WS studies 34 to 41. The other recently approved method, EPA 551, was only used minimally during WS 36 to 39. Participating laboratories chose "other" methods approximately 10 to 15 percent of the time.

Figure 16. Distribution of Analytical Techniques by WS Study: DBCP



b. Results of the PQL Analysis

For DBCP, the original PQL of 0.2 µg/L was derived by multiplying the detection limit of 0.02 µg/L by a factor of ten (56 FR 3551). Recent PE data from WS 26 to 41 have enabled EPA to attempt a reassessment of the PQL. Table 23 summarizes the data from these WS studies (except WS 28 and 33 which did not contain data), indicating the study number, the true value of the WS sample, the number of results from EPA and State laboratories, and the calculated percentage of laboratories whose results successfully passed within the 40 percent acceptance limits for DBCP.

Table 23. Evaluation of DBCP Data from WS Studies Using the ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 40% Acceptance Limits
36	0.196	50	92.0
32	0.233	24	95.8
39	0.246	36	91.7
37	0.286	42	88.1
34	0.363	45	88.9
38	0.429	48	97.9
41	0.451	34	100
40	0.527	50	98.0
35	0.589	29	93.1
27	0.653	18	88.9
29	0.980	39	94.9
26	1.13	35	88.6
31	1.78	44	97.7
30	2.65	24	91.7

Based on the data in Table 23, a revised PQL value could not be estimated because the passing rate of participating laboratories surpassed the 75 percent criterion needed. Also, the true values of the spiked samples in all but one study (WS 36) were greater than the existing PQL, limiting potential conclusions regarding a lower PQL. Therefore, a regression analysis was not performed. However, high passing rates at concentrations around the current PQL of 0.2 µg/L are suggestive of a change in the PQL.

Conclusion for DBCP

The MDL of EPA 504.1, a GC-microextraction technique, has not changed substantially since the promulgation of the NPDWR for DBCP. According to recent WS study data, laboratories have elected to use EPA 504.1 more often than EPA 551.1. These observations imply that detection limits for the overall contaminant have remained fairly constant over time. Using the data compiled from WS 26 to 41, the current PQL was reassessed. However, laboratories in all studies surpassed the 75 percent passing rate used in a PQL re-evaluation, such that a regression analysis was not attempted. Furthermore, the true value concentrations exhibited in almost all of the studies were higher than the current PQL, meaning that the effects

of lower PQL could not be determined. Although, the available PE data were not suitable to recalculate a new PQL, the high passing rates are suggestive of a change in the PQL.

1,4-Dichlorobenzene (para-dichlorobenzene)

Results of the Method Comparison

With the promulgation of the final rule for Phase I VOCs in July 1987 (52 FR 25690), five approved methods were listed for the determination of 1,4-dichlorobenzene (also known as para-dichlorobenzene) in drinking water: EPA Methods 502.1, 502.2, 503.1, 524.1, and 524.2. Since the promulgation of this rule, the Agency has removed EPA Methods 502.1, 503.1, and 524.1 from the list of approved methods. Table 24 summarizes the original and current methods and their MDLs.

Table 24. Results of the Analytical Methods Comparison for 1,4-Dichlorobenzene

MCL = 75 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL◊ (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 502.1[1]	Purge and Trap GC	ND•	EPA 502.2[2]	Purge and Trap GC	0.05 - 0.29
EPA 502.2[1]	Purge and Trap GC	0.01	EPA 524.2[2]	GC/MS	0.03 - 0.04
EPA 503.1[1]	Purge and Trap GC	0.006			
EPA 524.1[1]	GC/MS	2.0			
EPA 524.2[1]	GC/MS	0.03			

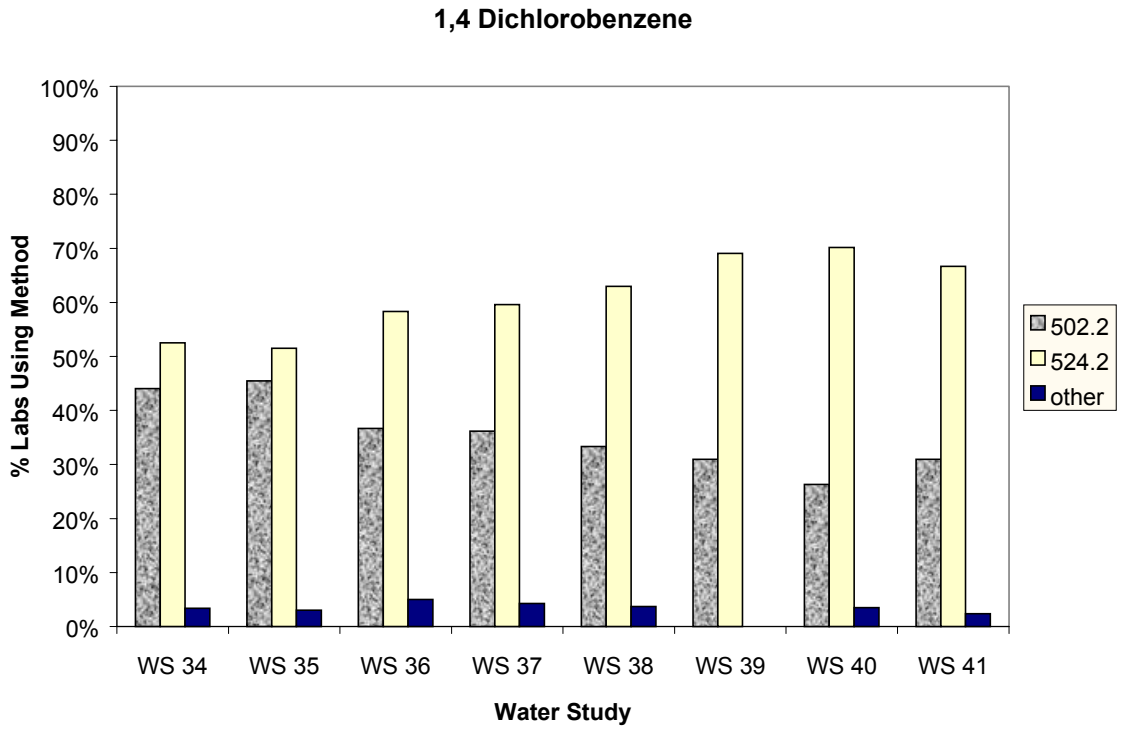
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for VOCs are listed at 40 CFR § 141.24(f)(17)
† Acceptance limits for organic compounds are listed at 40 CFR § 141.24(f)(17)(i)
• Not determined

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of different methods used by EPA and State laboratories during WS 34 to 41 is charted in Figure 17. The category of "other" methods includes those methods that were unknown or otherwise unidentified by the participating laboratories. During WS 34 to 41, the use of EPA 524.2 increased while use of EPA 502.2 diminished slightly.

Figure 17. Distribution of Analytical Techniques by WS Study: 1,4-Dichlorobenzene



b. Results of the PQL Analysis

The original PQL of 5 µg/L for 1,4-dichlorobenzene was determined by using PE data from Water Supply Studies 8 to 11 (50 FR 46880). For the six-year regulatory review, more recent WS data were compiled to provide a more accurate, updated assessment of laboratory capabilities. Hence, data from WS studies 24 to 27 and 29 to 41 were used to attempt to re-evaluate the PQL. Table 25 summarizes the available PE data by providing the study number, spiked value for the WS sample, number of laboratory results, and percentage of laboratories passing the proficiency test within the acceptance limits, meaning their reported results fall within the designated acceptance limits for a particular contaminant. The acceptance limits for 1,4-dichlorobenzene are ± 20 percent for a true value greater than 10 µg/L, or ± 40 percent for a true value lower than 10 µg/L (as specified at 40 CFR § 141.24(f)(17)(i)).

Table 25. Evaluation of 1,4-Dichlorobenzene Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
24	2.50	57		96.5
34	5.78	59		100
29	6.60	34		97.1
37	7.31	47		95.7
31	9.40	36		97.2
27	9.58	38		100
40	11.6	57	87.7	
36	11.9	60	95.0	
32	13.6	61	93.4	
38	14.2	54	55.6	
26	14.6	60	93.3	
33	15.1	33	87.9	
41	15.8	42	92.9	
30	16.1	58	84.5	
35	16.7	33	97.0	
39	17.8	42	88.1	
25	20.8	37	83.8	

Because a very large percentage of EPA and State laboratories passed the proficiency test within the bounds of the designated acceptance limits, the PQL could not be determined using the historical 75 percent criterion. Therefore, a regression analysis could not be conducted. However, the high passing rates suggest that the PQL could be lower.

Conclusion for 1,4-Dichlorobenzene

Since the promulgation of the NPDWR for 1,4-dichlorobenzene, the two analytical methods approved in 1987, EPA Methods 502.2 and EPA 524.2, are still approved for use today but are not more sensitive. According to the distribution of analytical methods usage over time, EPA 524.2 was more widely used than EPA 502.2 during WS 34 to 41. Upon review of the WS data, a high percentage of laboratories successfully passed the proficiency tests, preventing a graphical

estimated assessment of the PQL at the 75 percent passing rate. Although the available PE data are insufficient to recalculate the PQL, high passing rates are suggestive of a change in the PQL.

1,2-Dichloroethane

Results of the Method Comparison

The approved drinking water methods for the determination of 1,2-dichloroethane, a Phase I VOC (52 FR 25690). These methods all utilize GC or GC/MS with several extraction and/or detector variations: EPA Methods 502.1, 502.2, 503.1, 524.1, and 524.2. Since promulgation of these original methods, the Agency has removed EPA Methods 502.1, 503.1, and 524.1 from the list of approved methods, and has continued to approve the use of EPA methods 502.2 and 524.2. Table 26 summarizes the current and previous EPA methods along with their MDLs.

Table 26. Results of the Analytical Methods Comparison for 1,2-Dichloroethane

MCL = 5 µg/L **Current PQL = 5 µg/L** **DL▲ = 0.5 µg/L** **Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)**					
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL ◊ (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.002	EPA 502.2 [2]	Purge and Trap GC	0.07
EPA 502.2[1]	Purge and Trap GC	0.03	EPA 524.2 [2]	GC/MS	0.06
EPA 503.1 [1]	Purge and Trap GC	◊			
EPA 524.1[1]	GC/MS	0.2			
EPA 524.2[1]	GC/MS	0.06			

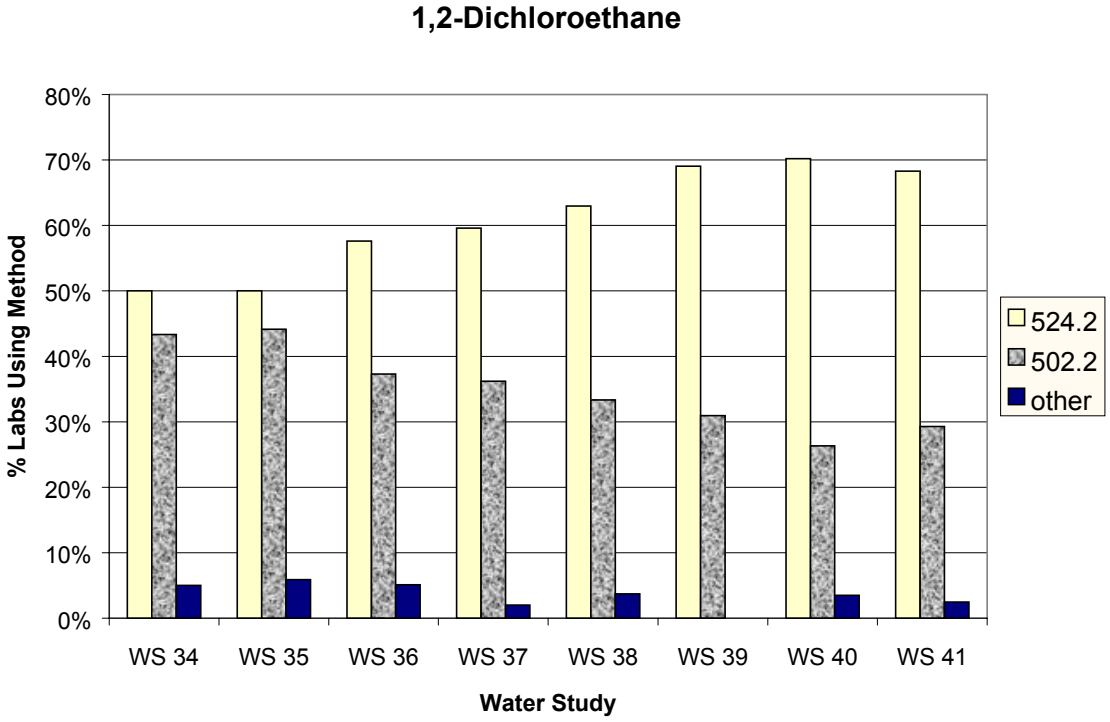
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for VOCs are listed at 40 CFR § 141.24(f)(17).
† Acceptance limits are listed at 40 CFR § 141.24(f)(17)(i)

Results of the Analysis of the WS Data

a. Method Usage Over Time

The types of methods used over time by the EPA and State laboratories during WS studies 34 to 41 are illustrated in Figure 18. The results for "other" techniques in this figure include any unknown or unreported methods. Using Figure 18, it is apparent that laboratories have increasingly relied on EPA 524.2 over EPA 502.2 to analyze for 1,2-dichloroethane. The percentage of labs using EPA 502.2 has steadily declined while EPA 524.2 has experienced an increase in use over the time period between WS studies 34 and 41.

Figure 18. Distribution of Analytical Techniques by WS Study: 1,2-Dichloroethane



b. Results of the PQL Analysis

The old PQL of 5 µg/L (52 FR 25700) for 1,2-dichloroethane was established by using the data from WS PE studies 8 to 11. To re-evaluate the PQL, data were taken from WS 24 to 41 (note that data was unavailable for WS 28). This data, including the study number, the spiked or "true" value for the WS sample, the number of laboratory results, and the percent of laboratories passing within the accepted limits of ± 20 percent for a spiked value of > 10 µg/L and ± 40 percent for a spiked value of < 10 µg/L, are compiled and illustrated in Table 27.

Table 27. Evaluation of 1,2-Dichloroethane Data from WS Studies Using Either 20% or 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limit	% Labs Passing ± 40% Acceptance Limit
27	4.88	37		100
30	7.69	59		98
36	9.00	59		100
31	9.25	36		100
26	10.8	59	95	
34	12.1	60	98	
29	12.9	34	79	
24	13.2	56	89	
37	13.2	47	81	
32	13.3	63	94	
41	13.7	41	93	
35	14.1	34	94	
25	15.5	38	90	
38	15.6	54	93	
40	15.6	57	88	
33	16.9	35	97	
39	17.6	42	86	

As shown in Table 27, the percentage of laboratories passing the acceptance limit averaged over 90 percent which is well above the 75 percent passing criterion selected to determine the PQL. Also, the spiked (or "true") values which the laboratories received were higher than the original PQL of 5 µg/L (with the exception of WS 27). Therefore, recalculation of the PQL could not be performed with these data. However, the high passing rates at concentrations close to the current PQL suggest that the PQL could be lower.

Conclusion for 1,2-Dichloroethane

Two new methods (EPA Methods 502.2 and 524.2) have been approved for the determination of 1,2-dichloroethane since promulgation of analytical methods under Phase I. One of the original methods, EPA 502.1, had the greatest detection sensitivity of the five methods mentioned but is currently not approved for analysis. The method usage evaluation

shows that, of the two currently approved methods, EPA 524.2 has steadily become the more preferred method of analysis by laboratories. Based on an analysis of the WS data, there are not enough appropriate data to conduct a reassessment of the PQL. However, high laboratory passing rates at concentrations close to the PQL 5 µg/L are suggestive of a change in the PQL.

1,1-Dichloroethylene

Results of the Method Comparison

The analytical methods approved for the determination of 1,1-dichloroethylene under the NPDWRs for Phase I VOCs include EPA Methods 502.1, 503.1, and 524.1 (52 FR 25899). Since the promulgation of the rule in 1987, the Agency has added EPA 245.2, to the list of approved methods. The currently approved methods for 1,1-dichloroethylene determination are EPA Methods 502.2 and 524.2. Table 28 summarizes the MDLs for both the original and current approved versions of the methods.

Table 28. Results of the Analytical Methods Comparison for 1,1-Dichloroethylene (Newly Promulgated Methods Indicated in Bold)

MCL = 7 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.003	**EPA 502.2[2]**	Purge and Trap GC	0.07
EPA 503.1[1]	Purge and Trap GC	0.2 - 0.5	**EPA 524.2[2]**	GC/MS	0.12
EPA 524.1[1]	GC/MS	0.2			

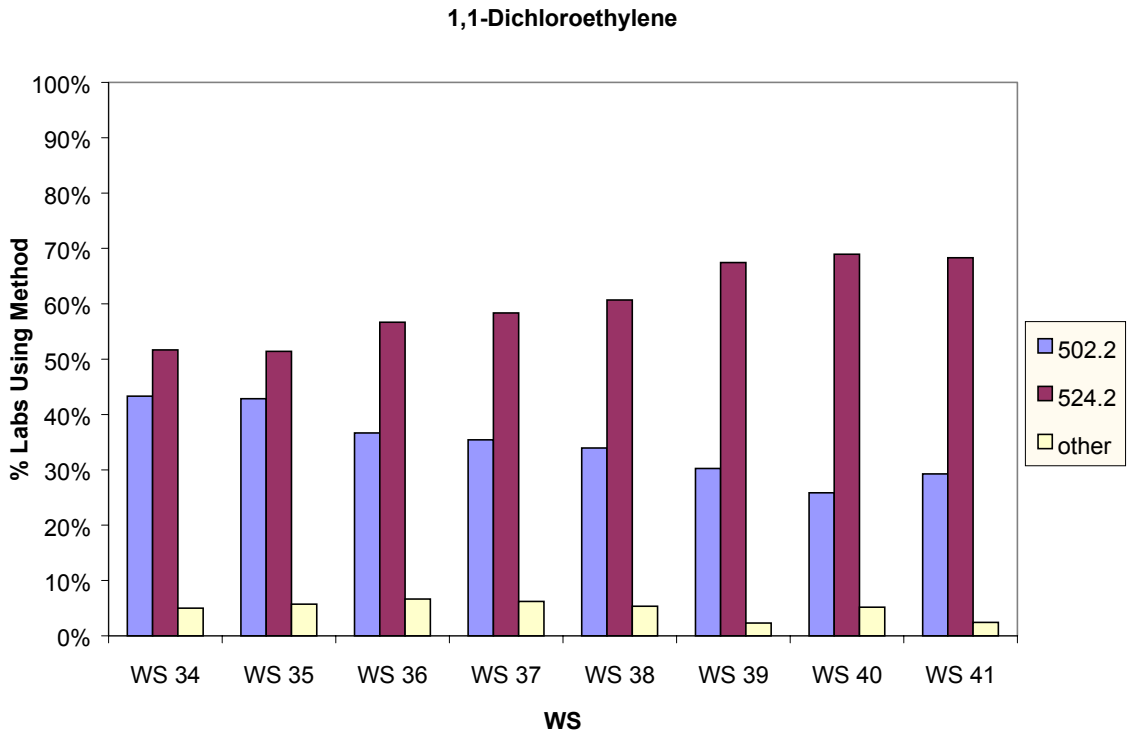
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17).
† Acceptance limits for VOCs are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 19 shows the distribution of analytical techniques used by EPA and State laboratories for WS studies 34 to 41. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as "unknown" methods, i.e., methods for which laboratories did not report any information on the type of method used. As shown in Figure 19, EPA 502.2 was used less as EPA 524.2 was used to most often (as shown from WS 34 to 41).

Figure 19. Distribution of Analytical Techniques by WS Study: 1,1-Dichloroethylene



b. Results of the PQL Analysis

The current PQL of 5 µg/L was originally set using previous PE data (54 FR 22102). With the availability of more current data from WS 24 to 41, a PQL re-evaluation was attempted. Table 29 summarizes the results of these studies, including the study number, the spiked (or "true") value for the sample, the number of laboratory results, and the percent of laboratories

passing the WS proficiency test for 1,1-dichloroethylene within the acceptance limits. The acceptance limits were calculated as ± 20 percent for a spike value of >10 µg/L and ± 40 percent for a spiked value of <10 µg/L (as specified at 40 CFR §141.23(f)(17)(i)).

Table 29. Evaluation of 1,1-Dichloroethylene Data from WS Studies Using Either 20% or 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
41	5.25	41		97.6
24	5.36	57		87.7
26	6.64	60		95.0
31	7.02	37		97.3
34	7.64	60		98.3
36	8.49	60		98.3
32	9.13	63		100
27	9.45	37		89.2
29	11.7	35	74.3	
38	11.7	56	19.6	
39	12.4	43	79.1	
33	12.9	33	75.8	
35	13.9	35	88.6	
30	14.2	45	77.8	
25	14.9	38	94.7	
37	16.5	48	83.3	
40	18.3	58	86.2	

The data from the available PE studies were not conducive to PQL re-evaluation, as the percentage of labs passing generally exceeded the standard 75 percent passing criterion needed to estimate the PQL using the graphical approach (with the exception of two studies). However, high laboratory passing rates for those spike concentrations just above the PQL of 5 µg/L suggest that the PQL could be lower.

Conclusion for 1,1-Dichloroethylene

The method comparison results indicate that EPA 502.2 is now the most sensitive method for determination of 1,1-dichloroethylene in drinking water. As revealed by the results of method usage over time, EPA 524.2 is the most commonly employed method for 1,1-dichloroethylene determination in recent PE studies. Based on the evaluation of more recent quantitative PE data, a recalculation of the PQL is not possible. However, the high laboratory passing rates for a couple spike samples with concentrations slightly above the current PQL of 5 µg/L suggest that the PQL could change.

Dichloromethane (methylene chloride)

Results of the Method Comparison

At the promulgation of the Phase V rule for VOCs (57 FR 31776), four analytical methods were approved (EPA Methods 502.1, 502.2, 524.1, and 524.2) for the analysis of dichloromethane (also known as methylene chloride). Since that time, EPA Methods 502.1 and 524.1 have been removed from the approved list, leaving EPA Methods 502.2 and 524.2 as the remaining currently approved methods; no new methods have been introduced. Table 30 provides descriptions of the methods and their MDLs. The MDLs of the two current methods remain unchanged from their values at the promulgation of the rule.

Table 30. Results of the Analytical Methods Comparison for Dichloromethane

MCL = 5 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	unknown	EPA 502.2[2]	Purge and Trap GC	0.02
EPA 502.2[1]	Purge and Trap GC	0.02	EPA 524.2[2]	GC/MS	0.03
EPA 524.1[1]	GC/MS	0.13 - 0.25*			
EPA 524.2[1]	GC/MS	0.03			

[1] "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water," June 1985.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLS for organic compounds are listed at 40 CFR 141.24(f)(17).

† Acceptance limits for VOCs are listed at 40 CFR 141.24(f)(17)(i).

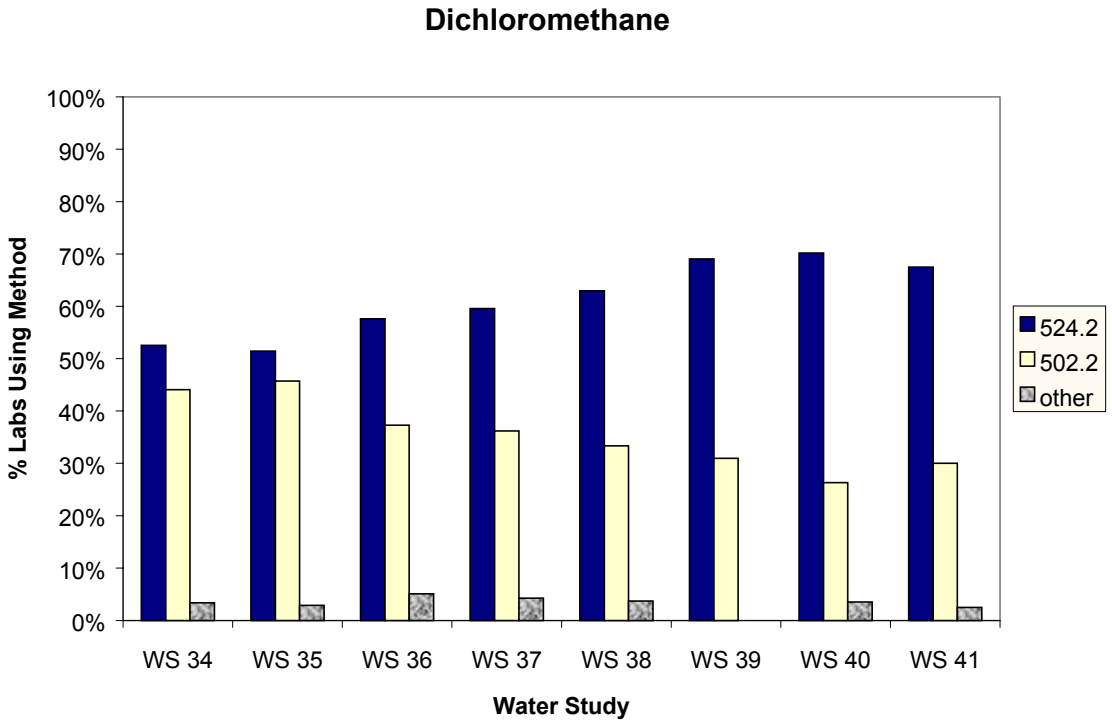
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation, and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of methods used over WS studies 34 to 41 is illustrated in Figure 20. The designation "other" includes all unknown and unreported methods. As illustrated in Figure 20, EPA 524.2 was the predominant method used in these WS studies. Since WS 35, EPA 524.2 has steadily increased in its usage, experiencing only a slight decrease in WS 41. Even though EPA 502.2 features slightly better sensitivity than EPA 524.2, laboratories favored EPA 524.2, which utilizes GC/MS.

Figure 20. Distribution of Analytical Techniques by WS Study: Dichloromethane



b. Results of the PQL Analysis

Table 31 summarizes the results of the data from WS 24 to 41 for the use in the PQL re-evaluation. Note that data for WS 24, 25, 27, 28, 30, and 31 are not available for this analysis. Table 31 includes the WS number, the spiked "true" value, number of labs that participated in the studies, and the percentage of those passing within the acceptance limit designated for dichloromethane (± 20 percent if spiked "true" value is > 10 µg/L or ± 40 percent if the spiked "true" value is < 10 µg/L specified at 141.24(f)(17)(i)).

Table 31. Evaluation of Dichloromethane Data from WS Studies Using Either 20% or 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
35	5.83	35		97
40	6.2	57		97
39	7.31	42		100
32	7.77	51		94
37	8.41	47		92
36	12.3	59	90	
33	12.8	34	94	
38	14.7	54	98	
29	14.7	33	97	
26	15.2	51	71	
41	15.9	40	85	
34	18.4	59	86	

The original PQL of 5 µg/L was derived from PE data from WS 22, 23, and 26 (57 FR 60953). As shown by Table 30, the WS data are not appropriate for a PQL re-evaluation using the linear regression approach. For most of the concentrations listed in Table 31, the percentage of laboratories passing were well above the 75 percent criterion necessary to recalculate the PQL. In summary, these data were not suitable for use in reassessing the current PQL using a graphical method. However, high laboratory passing rates at concentrations close to the current PQL suggest that the PQL may be lower.

Conclusion for Dichloromethane

Since the promulgation of the Phase V rule, no new methods have been approved for the analysis of dichloromethane, and analytical capabilities have remained essentially constant. Of the currently approved methods, EPA 524.2 is used more frequently by laboratories for the detection of dichloromethane, although it is not the most sensitive method available (EPA 502.2). During WS 24 to 41, the percentage of laboratories passing was very high, limiting the possibilities of re-evaluating the PQL using the historical 75 percent criterion. Although, data are insufficient to recalculate the PQL, high passing rates at values close to the current PQL suggest that the PQL could change.

1,2-Dichloropropane

Results of the Method Comparison

The final NPDWR for 1,2-dichloropropane, a Phase II VOC, has four approved methods: EPA Methods 502.1, 502.2, 524.1, and 524.2. Since that time, EPA Methods 502.1 and 524.1 have been removed from the approved list, leaving EPA Methods 502.2 and 524.2 as the remaining currently approved methods; no new methods have been introduced. Table 32 provides descriptions of the methods and their MDLs. The MDLs of the two current methods remain essentially unchanged from their values at the promulgation of the rule.

Table 32. Results of the Analytical Methods Comparison for 1,2-Dichloropropane (Newly Promulgated Methods in Bold)

MCL = 5 µg/L Current PQL = 5 µg/L DL^ = 0.5 µg/L Acceptance Limits† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 502.1[1]	Purge and Trap GC	N.D.	EPA 502.2[2]	Purge and Trap GC	0.02 - 0.03
EPA 502.2[1]	Purge and Trap GC	0.01	EPA 524.2[2]	GC/MS	0.02 - 0.04
EPA 524.1[1]	GC/MS	0.2			
EPA 524.2[1]	GC/MS	0.02 - 0.04			

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

N.D. = Not determined

▲ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17).

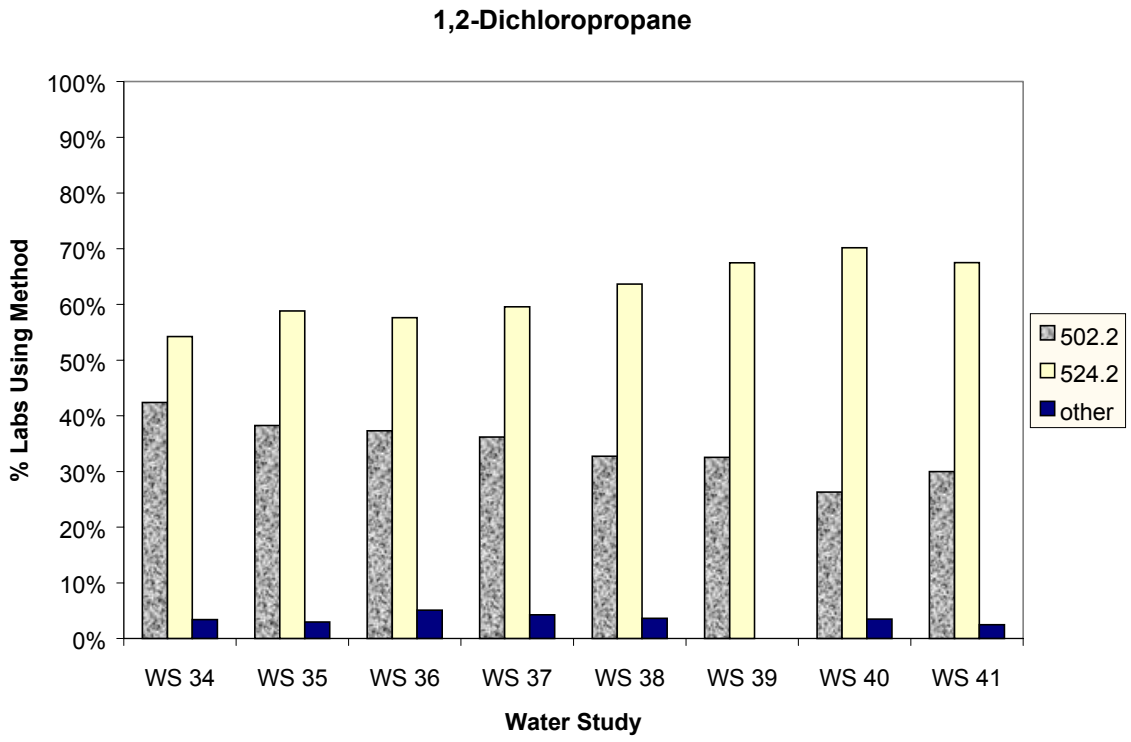
† Acceptance limits for VOCs are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

For PE WS studies 34 to 41, the distribution of methods used by EPA and State laboratories is illustrated by Figure 21. The category of "other" contains those methods that were unknown or unidentified by participating laboratories. As Figure 21 shows, EPA 524.2 was the preferred method for laboratories participating in WS 34 to 41. For the most part, the use of EPA 502.2 decreased over time.

Figure 21. Distribution of Analytical Techniques by WS Study: 1,2-Dichloropropane



b. Results of the PQL Analysis

The original PQL of 5 µg/L (56 FR 3526) for 1,2-dichloropropane was determined by using PE data from WS 18. A re-evaluation of the PQL was attempted using more recent data from WS studies 29 through 41. Table 33 summarizes the results of these WS studies, including the study number, the true value concentration of the spiked sample, the number of laboratory results returned, and the percentage of laboratories passing the proficiency test within acceptance limits of ± 20 percent for a true value greater than 10 µg/L, or ± 40 percent for a true value lower than 10 µg/L (as specified in 141.24(f)(17)).

Table 33. Evaluation of 1,2-Dichloropropane Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
32	6.46	61		100
35	9.00	34		100
30	10.9	58	98.3	
39	12.2	43	93.0	
34	12.3	59	96.6	
37	14.2	47	91.5	
33	14.3	32	93.8	
41	15.4	40	97.5	
29	15.8	33	87.9	
36	16.4	59	93.2	
38	18.3	55	94.5	
40	19.0	57	94.7	

For this contaminant, the participating laboratories studies achieved success rates far greater than the 75 percent criterion typically used to estimate the PQL. Also, all of the true value concentrations used in the available studies exceeded the current PQL. Thus, the PQL could not be re-evaluated using the regression method. However, high passing rates of 100 percent for WS 32 with a spike concentration of 6.46 µg/L is very close to the current PQL. This suggests that the PQL could be lower.

Conclusion for 1,2-Dichloropropane

The method comparison results show that no new methods have been approved since the promulgation of the NPDWR for 1,2-dichloropropane. Evaluation of the quantitative PE data showed that laboratories conducting WS analyses had surpassed the 75 percent criterion. Because the data featured a large percentage of laboratories passing, and very high true value concentrations, a re-evaluation of the PQL could not be performed using the typical graphical estimation approach. Thus, the available WS data are insufficient to recalculate the PQL for 1,2-dichloropropane. However, high laboratory passing rates for WS studies with concentrations close to the current PQL are suggestive of a change in the PQL.

2,3,7,8-TCDD (Dioxin)

Results of the Method Comparison

2,3,7,8-TCDD, commonly known as dioxin, was listed with the Phase V SOCs (57 FR 31776). Dioxin has not had any new methods approved for analysis since the promulgation of the NPDWRs for this contaminant. However, the MDL for EPA 1613 has changed from 5 pg/L (picogram = 10^{-12} gram) to 1 pg/L, indicating a slight increase in sensitivity. Table 34 shows the specifications of Method 1613 in both past and current periods.

Table 34. Results of the Analytical Methods Comparison for 2,3,7,8-TCDD

MCL = 30 pg/L	Current PQL = 30 pg/L		DL[▲] = 5 pg/L	Acceptance Limit[†] = ± 2*S.D.	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (pg/L)**	**Method**	**Technique**	**MDL (pg/L)**
EPA 1613[1]	GC/MS	5	EPA 1613[2]	GC/MS	1

[1] Method 1613, Revision A, USEPA, April 1990.

[2] Method 1613, "Tetra-through Octa-chlorinated Dioxins and Furans by Isotope-Dilution HRGC/HRMS," EPA/821-B-94-005, October 1994.

[▲] Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

[†] Acceptance limits for organic compounds are listed at 40 CFR 141.24(h)(19)(i).

Results of the Analysis of the WS Data

WS data were not available for dioxin; hence, no analyses on these data could be performed.

Conclusion

No new methods have been approved for the analysis of dioxin since the promulgation of the NPDWRs. However, the sensitivity of Method 1613 has slightly increased from 5 to 1 pg/L since that time. A re-evaluation of the PQL could not be determined because no PE data were available for examination. Therefore, the current PQL is likely to remain unchanged.

Diquat

Results of the Method Comparison

Diquat became a regulated SDWA contaminant with the promulgation of the July 1992 Phase V rule for SOCs. Table 35 compares the approved methods at promulgation with currently approved methods. At the time of the Phase V regulation only one method, EPA 549, was approved for determination of diquat in drinking water (57 FR 31776). In August 1992, EPA 549 was replaced by an updated method, EPA 549.1 ("Methods for the Determination of Organic Compounds in Drinking Water--Supplement 2"). Because EPA 549.1 received approval so soon after the promulgation of the Phase V rule, it is listed in the column of methods approved at promulgation in Table 35. In 1999 EPA approved EPA 549.2 (64 FR 67450) and discontinued EPA 549.1. The MDL of EPA Method 549.2 is approximately five times more sensitive than the original version of the method (EPA 549).

Table 35. Results of the Analytical Methods Comparison for Diquat (Newly Promulgated Methods Are Indicated in Bold)

MCL = 20 µg/L	**Current PQL = 4 µg/L**		**DL▲ = 0.4 µg/L**	**Acceptance Limit† = ± 2*S.D.**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 549[1]	LSE, HPLC with UV	4	**EPA 549.2**[3]	LSE, HPLC with photodiode array UV detector	0.72
EPA 549.1[2]	LSE, HPLC with UV	0.44 - 0.51*			

[1] "Methods for the Determination of Organic Compounds in Drinking Water–Supplement I," EPA-600/4-90/020, July 1990.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement II," EPA/600/R-92/129, August 1992. (Note this method was not actually approved at the time of July 1992 Phase V promulgation but was approved immediately after.)

[3] "Analytical Methods for Chemical and Microbiological Contaminants and Revisions to Laboratory Certification Requirements ," *Federal Register*, Vol. 64, No. 230, pp. 67450-67467.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

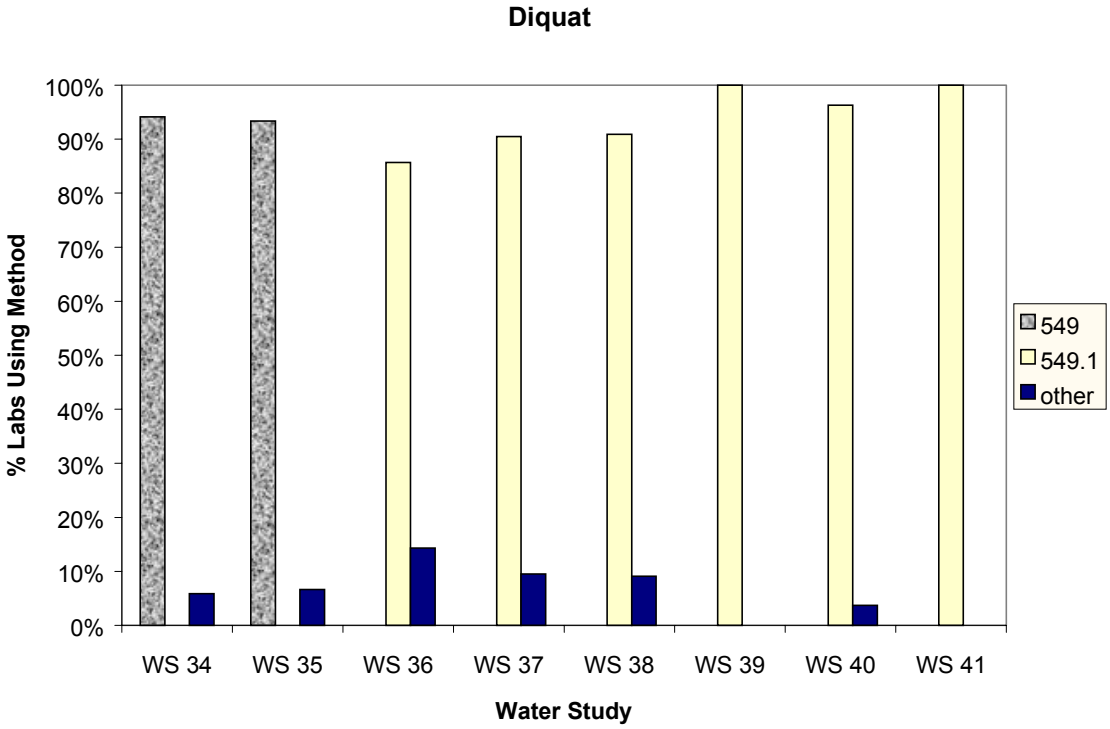
†Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of analytical techniques used by the EPA and State laboratories in WS 34 to 41 is shown in Figure 22. The "other" techniques represent methods which were not specifically identified by participating laboratories or were otherwise unknown. EPA has consistently approved a single method for diquat at any given time, EPA Method 549 was predominantly used prior to WS 36 and EPA 549.1 was used predominantly after WS 36.

Figure 22. Distribution of Analytical Techniques by WS Study: Diquat



b. Results of the PQL Analysis

The original PQL for diquat (4 µg/L) was derived by using PE data from WS 23 to 27 (56 FR 60949). A reassessment of the PQL was attempted after compiling additional data from WS 24 to 41. However, for several of these available water studies, the number of participating laboratories were too few (under ten) to include for consideration in the analysis. After omitting these studies, the remaining usable PE data were summarized, including the study number, the true value of the WS sample, the number of results from EPA and State laboratories, and the calculated percentage of laboratories whose results successfully passed within federally

designated acceptance limits (Table 35). The acceptance limits for diquat are specified in 40 CFR §141.24(h)(19)(i) to be twice the standard deviation, or ± 2*S.D., from the value "x" (where x = aT+b and T represents the true value).

Table 36 reveals that laboratory success rates ranged between 78.6 and 100 percent. Thus, use of the 75 percent criterion for estimation of the PQL by the graphical method would be meaningless. The dataset is also incompatible with the goals of a PQL reassessment–particularly a potential lowering of the PQL–because the concentrations of all the spiked samples exceeded the current PQL. Also, the concentration of the spike samples was well above the PQL of 5 µg/L.

Table 36. Evaluation of Diquat Data from WS Studies Using the ± 2* S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 2* S.D. Acceptance Limits
37	8.41	21	90.5
36	14.7	28	78.6
40	14.8	27	96.3
38	23.7	22	95.5
32	28.2	11	100
34	29.2	17	94.1
39	32.2	21	95.2
35	37.4	15	86.7
41	44.0	17	100

Conclusion for Diquat

As shown by the results of the method comparison, few methods have been approved by EPA for the determination of diquat. The analytical technology supporting the determination of diquat has remained essentially unchanged over time. However, analytical capabilities have improved. The original method, EPA 549, was much less sensitive than today's method, EPA 549.2, indicating significant improvement. The plot of method usage over time reveals that the techniques predominantly used by participating laboratories were EPA Methods 549 (prior to WS 36) and 549.1 (subsequent to WS 36). Although the method comparison indicates increased analytical capabilities, the available WS data did not provide information suitable for a PQL

reassessment. The percentage of laboratories passing within the acceptance window was generally well above the 75 percent criterion for use in the linear regression approach.

Ethylene Dibromide

Results of the Method Comparison

With the Phase II SOCs (56 FR 3526), EPA 504, was the only approved method listed for analysis of ethylene dibromide (EDB) in drinking water. Since this regulation was promulgated, the Agency has approved a new revision of GC with microextraction (EPA 504.1) and approved an additional analytical method (EPA 551.1, GC with LLE and ECD). As shown in Table 37, the MDLs of EPA Methods 504 and 504.1 are essentially equivalent, but EPA 551.1 offers a slightly greater level of sensitivity.

Table 37. Results of the Analytical Methods Comparison for Ethylene Dibromide (New Methods in Bold)

MCL = 0.05 µg/L Current PQL = 0.05 µg/L DL▲ = 0.01 µg/L Acceptance Limit† = ± 40%					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 504[1]	Microextraction, GC	0.01	**EPA 504.1[2]**	Microextraction, GC	0.01
			EPA 551.1[2]	LLE/GC w/ ECD	0.008

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

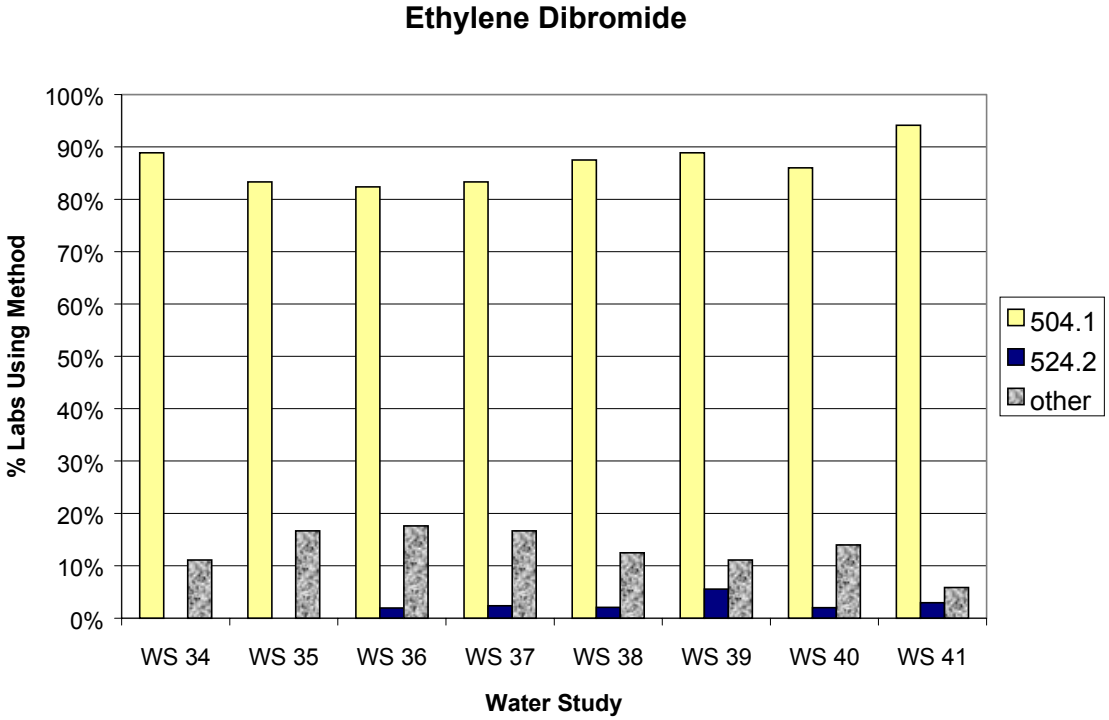
† Acceptance limits are listed at 40 CFR §141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 23 illustrates the distribution of the analytical techniques used by the EPA and State laboratories in WS studies 34 to 41. The "other" designation includes methods for which laboratories did not report any information on the method used or non-EPA methods. The use of EPA 504.1 greatly exceeds the use of any other method. This distribution is consistent through the duration of the WS studies shown in Figure 23.

Figure 23. Distribution of Analytical Techniques by WS Study: Ethylene Dibromide



b. Results of the PQL Analysis

The current PQL, 0.05 µg/L, was derived from a multiplier of 5 from the MDL of 0.01 µg/L (56 FR 3552). The data used for PQL re-evaluation were taken from WS studies 24 to 41. Table 38 summarizes the results of the WS studies, providing the study number, the true concentration of the spiked sample, the number of laboratories participating, and the percentage of laboratories passing the WS study (evaluated using acceptance limit of ± 40 percent for EDB as cited in 40 CFR § 141.24(h)(19)(i)).

Using the 75 percent criterion, it appears from the numerical data that EPA and regional laboratories are able to achieve acceptable results within the ± 40 percent acceptance window at concentrations from 0.14 to 2.3 µg/L.

Table 38. Evaluation of Ethylene Dibromide Data from WS Studies Using the ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing Acceptance Limits
37	0.138	42	81
33	0.143	24	75
39	0.227	36	94
36	0.283	51	94
38	0.336	48	96
41	0.344	34	100
34	0.406	45	87
26	0.434	35	91
24	0.480	32	100
35	0.609	30	90
31	0.637	25	84
40	0.638	50	98
29	0.850	25	84
25	0.944	18	100
30	1.39	39	92
27	1.45	17	88
32	2.29	44	98

The percentages of the acceptable results for laboratories were not plotted, as these values all exceeded the 75 percent criterion and therefore could not contribute meaningful information toward the re-evaluation of a PQL using the linear regression approach. In addition, none of the WS studies evaluated had spike concentrations below the current PQL of 0.05 µg/L. However, WS studies at concentrations slightly above the PQL (WS 37 and 33) had laboratory passing

rates of 81 and 75 percent, respectively. This would indicate that the current PQL is probably appropriate and unlikely to change.

Conclusion for Ethylene Dibromide

The method comparison results indicate that the sensitivity of the available methods has not improved significantly since the promulgation of NPDWRs for EDB. Evaluation of more recent WS data provides no evidence that would support a change from the current PQL of 0.05 µg/L.

Fluoride

Results of the Method Comparison

Fluoride, a Phase II IOC, is unique among SDWA contaminants because it is often added to drinking water to provide well-known health benefits. Because low concentrations of fluoride are often added to public water supplies to protect dental health, EPA has not published a detection limit for this contaminant. Since the Agency's promulgation of the MCL for fluoride (April 1986, 51 FR 11397), this contaminant has gained several additional approved methods, mostly developed by voluntary consensus standard organizations. Currently, the only EPA-approved method for fluoride determination is EPA 300.0, an ion chromatography method with greater sensitivity than the EPA methods approved at the time of promulgation. Table 39 summarizes original and current methods, and their individual detection limits. The voluntary consensus standard method MDLs are not listed in this table because non-EPA methods are not required to document detection limits.

Table 39. Results of the Analytical Methods Comparison for Fluoride

MCL = 4 mg/L	**Current PQL = 0.5 mg/L**		**DL = N/A▲**	**Acceptance Limit† = ± 10%**	
Methods Approved At Promulgation			**Currently Approved Methods (141.23)**		
Method	**Technique**	**MDL (mg/L)**	**Method**	**Technique**	**MDL (mg/L)**
EPA 340.1[1]	Colorimetric SPADNS, with Bellack Distillation	0. 1- 1.4*	**EPA 300.0**[6]	Ion chromatography	0.01
EPA 340.2[1]	Potentiometric, with ion-selective electrode (ISE)	NA ▲			
EPA 340.3[1]	Automated Alizarin, with distillation (complexone)	0.05 - 1.5*			

D1179-72A[2]	Colorimetric SPADNS, with distillation	N/A ‘	**D1179-93B**[7]	Manual electrode	N/A ‘
D1179-872B[2]	Potentiometric, with ISE	N/A ‘	**D4327-91**[8]	Ion chromatography	N/A ‘
414A; C[3]	Colorimetric SPADNS, with distillation	N/A ‘	**4500F-B,D**[8]	Manual distillation; colorimetric SPADNS	N/A ‘
414B[3]	Potentiometric, with ISE	N/A ‘	**4500F-C**[8]	Manual electrode	N/A ‘
413E[3]	Automated Alizarin, w/distillation	N/A ‘	**4500F-E**[8]	Automated Alizarin	N/A ‘
			4110B[8]	Ion chromatography	N/A ‘
129-71W[4]	Automated Alizarin, w/distillation	N/A ‘	129-71W[4]	Automated Alizarin	N/A‘
380-75WE[5]	Automated electrode	N/A ‘	380-75WE[5]	Automated electrode	N/A‘

[1] "Methods of Chemical Analysis of Water and Wastes (MCAWW)," EPA/600/4-79-020, EPA Environmental Monitoring Laboratory, Cincinnati, Ohio 45268. March 1983.

[2] *Annual Book of ASTM Standards*, part 31, Water. American Society for Testing and Materials, 1961 Race Street. Philadelphia, PA 19103.

[3] *Standard Methods for the Examination of Water and Wastewater*, 16th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1985.

[4] "Fluoride in Water and Wastewater, Industrial Method 129-71W," Technicon Industrial Systems, Tarrytown, New York 10591. December 1972.

[5] "Fluoride in Water and Wastewater," Technicon Industrial Systems, Tarrytown, New York 10591. February 1976.

[6] "Methods for the Determination of Metals in Environmental Samples Supplement 1," EPA/600/R-94/111, May 1994.

[7] *Annual Book of ASTM Standards*, Vol. 11.01. American Society for Testing and Materials, 1961 Race Street. Philadelphia, PA 19103.

[8] *Standard Methods for the Examination of Water and Wastewater*, 19th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation.

‘ N/A: not available. See above text for explanation.

† Acceptance limits for inorganic compounds are listed at 40 CFR §141.23(k)(3)(ii).

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

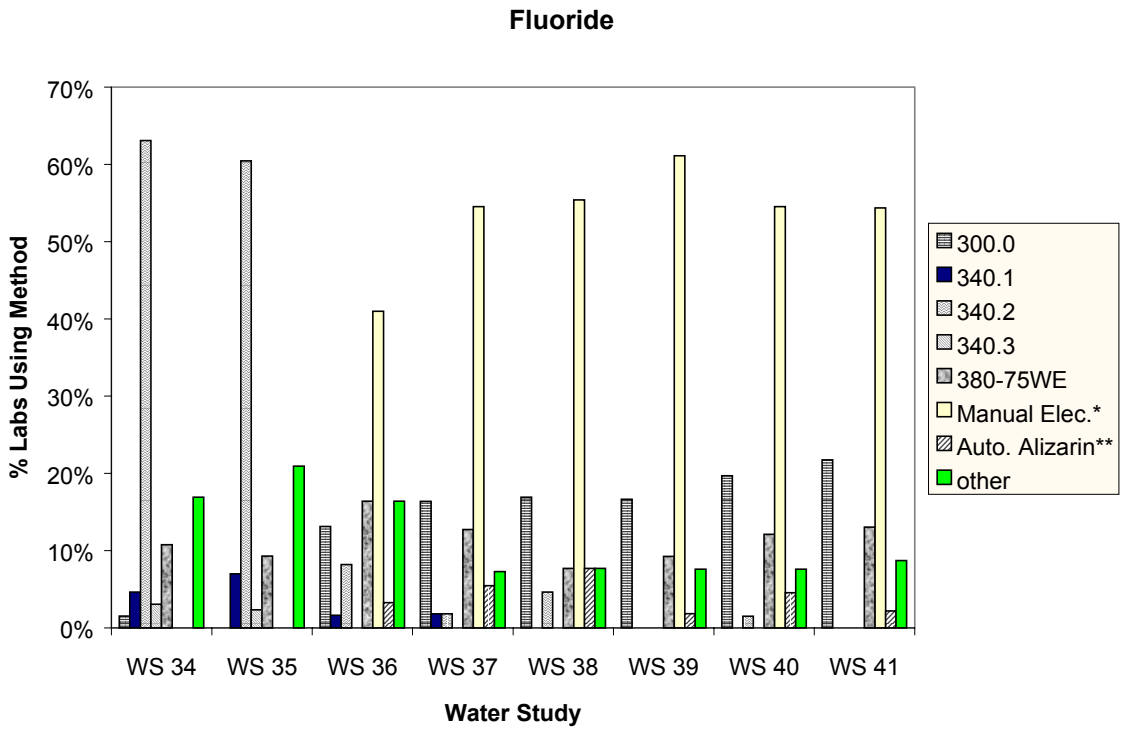
As shown in Table 39, multiple versions of methods exist for some technologies such as ion chromatography, automated electrode, automated alizarin, and manual electrode.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the analytical techniques used by the EPA and State laboratories in WS 34 to 41 is shown in Figure 24. The results for "other" techniques include the use of other techniques identified by the laboratories participating in the WS study, as well as "unknown" methods, i.e., methods for which laboratories did not report any information on the type of method used.

Figure 24. Distribution of Analytical Techniques by WS Study: Fluoride



* Manual electrode combines the methods D1179-93B (ASTM) and 4500F-C (SM).

** Automated Alizarin combines the methods 4500F-E (SM) and 129-71W (Technicon).

Fluoride determination has involved the use of a wide variety of analytical methods. In earlier years, the most popular method was EPA 340.2, an ion selective electrode method, but its usage dropped significantly after WS 36. Since WS 36, method usage by laboratories participating in the water supply studies has been dominated by a non-EPA manual electrode method. Laboratories have also increasingly favored the use of EPA 300.0, though to a lesser extent relative to the manual electrode methods (D1179-93B, 4500F-C). A small fraction of

participating laboratories have employed the voluntary consensus standard method 380-75WE (automated electrode) throughout WS 34 to 41.

b. Results of the PQL Analysis

The current PQL (500 µg/L or 0.5 mg/L) was originally determined from older PE water supply study data (WS 8 to 12, see USEPA, "Monitoring for Fluoride in Drinking Water: Revised," March 1986). The PQL was re-evaluated using a broader range of PE data including more recent studies (WS 24 to 41). Table 40 summarizes the results of these studies, providing the study number, the spiked or "true" value for the WS sample, the number of results from EPA and State laboratories, and the actual responses returned by laboratories. For fluoride, EPA stipulates acceptance limits of ± 10 percent (§141.23(k)(3)(ii)).

Table 40. Evaluation of Fluoride Data from WS Studies Using the 10% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (mg/L)	# Results from EPA and State Labs	% Labs Passing ± 10% Acceptance Limits
29	0.33	33	84.8
34	1.10	65	93.8
26a	1.25	63	93.7
24b	1.30	62	96.8
40	1.40	66	60.6
25b	1.50	40	87.5
24a	1.72	62	93.5
37	1.80	55	87.3
32	2.00	67	92.5
25a	2.50	40	87.5
39	2.90	54	92.6
26b	3.41	64	89.1
35	3.80	43	97.7
27	4.35	37	86.5
38	4.70	65	98.5

WS #	Spiked "True" Value (mg/L)	# Results from EPA and State Labs	% Labs Passing ± 10% Acceptance Limits
31	5.70	33	97.0
41	6.20	46	95.3
33	6.60	35	94.3
36	7.20	61	95.1
30	7.90	61	93.4

The WS data indicate that EPA and State laboratories performed with high success rates in WS studies involving fluoride determination. On average, 91 percent of participating laboratories achieved results within the ± 10 percent acceptance window. The range of true value concentrations contained many spikes above the current PQL (0.5 mg/L), preventing a thorough analysis of laboratory capabilities at or below the PQL. For WS 29, the only study where the true value was below the PQL, 85 percent of laboratories successfully passed within the specified acceptance limits, well above the 75 percent criterion. Thus, it might be possible for laboratories to pass the PE studies at even lower concentrations; however, such a conclusion is uncertain in the absence of additional data below the PQL value.

Conclusion for Fluoride

The MDL of the only currently approved EPA method, EPA 300.0, is much lower than those of previous EPA methods and use of this method has increased gradually over time. However, EPA 300.0 still accounts for less than a quarter of method usage for fluoride and thus cannot be representative of overall laboratory analytical capabilities. Based on the graph of method usage over time (Figure 24), the method most commonly used in recent years is a manual electrode method, whose detection limit is not specified. Hence, the combined results of the method comparison and method usage over time suggest that analytical capabilities have improved for only a subset of EPA and State laboratories.

Based on the evaluation of quantitative WS data, the current PQL of 0.5 mg/L is still supportable and appropriate, although an even lower value might be attainable based on the high success rates of laboratories in water studies. However, this hypothesis would require further analysis using WS data at spiked concentrations below 0.5 mg/L, and such data are currently not available.

Glyphosate

Results of the Method Comparison

In 1992, the Agency listed EPA 547 as the only approved method for determination of glyphosate in drinking water, according to the Phase V rule for SOCs (57 FR 31776). Since that time, EPA has added Standard Method (SM) 6651, a voluntary consensus standard method, to the approved list. The MDL of SM 6651 is not specified, but it is reasonable to expect a similar detection limit compared to EPA 547 due to the similarity in determinative technique. Because the MDL of EPA 547 has not changed over time and no additional EPA methods were approved, the analytical capabilities for determination of glyphosate have remained constant since the approval of EPA 547.

Table 41. Results of the Analytical Methods Comparison for Glyphosate (Newly Promulgated Methods are Indicated in Bold)

MCL = 0.7 mg/L	**Current PQL = 0.06 mg/L**		**DL▲ = 0.006 mg/L**	**Acceptance Limit† = ± 2*S.D.**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (mg/L)**	**Method**	**Technique**	**MDL (mg/L)**
EPA 547[1]	HPLC, post-column derivatization, fluorescence detection	0.006	EPA 547[1]	HPLC, post-column derivatization, fluorescence detection	0.006
			SM 6651[2]	Liquid chromatography, post-column fluorescence	N/A◇

[1] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement I," EPA/600/4-90/020, July 1990.

[2] *Standard Methods for the Examination of Water and Wastewater*. 18th edition. American Public Health Association, 1015 Fifteenth Street NW, Washington, DC 20005.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

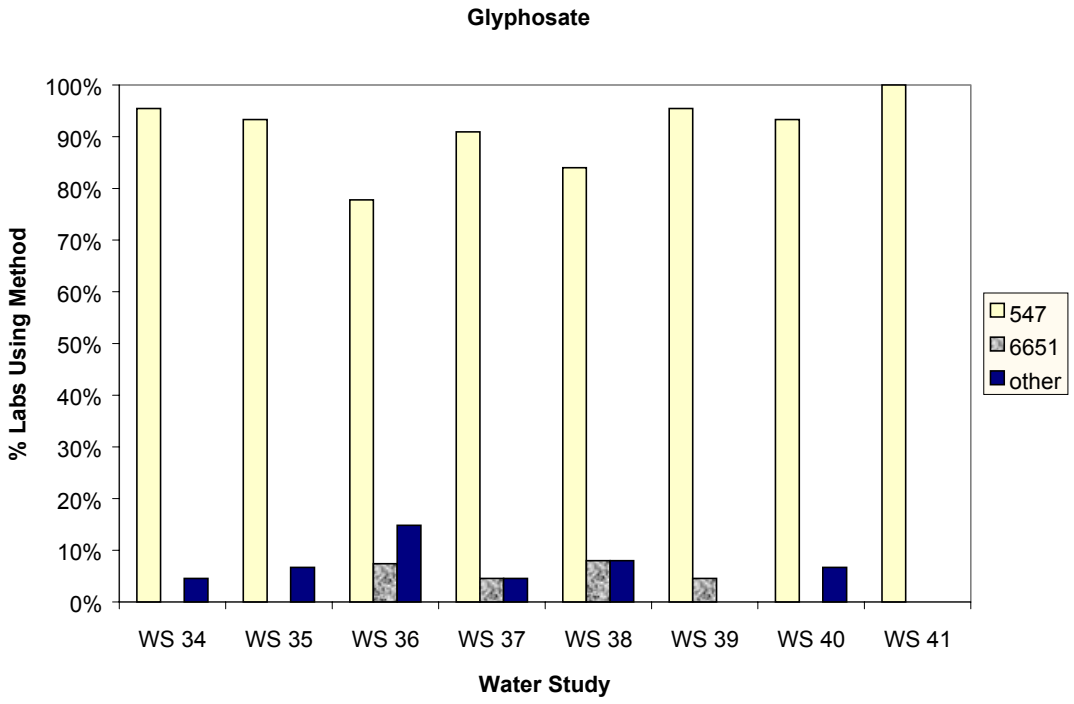
◇ N/A = not available. MDLs are not necessarily specified for non-EPA methods.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 25 is a plot of the distribution of analytical techniques used by the EPA and State laboratories during WS 34 to 41. As shown in Figure 25, the majority of the participating laboratories utilized EPA 547 for the determination of glyphosate. A small fraction of laboratories employed the voluntary consensus standard method, SM 6651 and a minority of laboratories used "other" methods or methods that were not specified.

Figure 25. Distribution of Analytical Techniques by WS Study: Glyphosate



b. Results of the PQL Analysis

Glyphosate currently has a PQL of 0.06 mg/L (or 60 µg/L) which was derived from previous WS results from EPA and State laboratories (WS 24 to 27, 56 FR 60949). In light of the availability of more recent PE WS data from WS studies 32 to 41, efforts were made to reassess the PQL. Table 42 summarizes the data from these water studies, indicating the study number, the true value of the WS sample, the number of results from laboratories, and the calculated percentage of laboratories whose results successfully passed within the designated acceptance limits for glyphosate (± 2*S.D. as specified at 141.24(h)(19)(i).

Table 42 shows that the laboratories in these water studies were able to achieve results within the acceptance window with 73 to100 percent passing rates. Using the 75 percent criterion for estimation of the PQL will not be meaningful for this dataset because of the high success rate and the lack of spike values at concentrations around the current PQL of 60 µg/L.

Table 42. Evaluation of Glyphosate Data from WS Studies Using the ± 2* S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 2*S.D. Acceptance Limits
33	308	11	72.7
40	375	30	96.7
38	410	25	88.0
34	438	22	90.9
32	447	15	86.7
36	528	27	96.3
41	560	17	100
39	620	22	95.5
35	665	15	86.7
37	780	22	77.3

Conclusion for Glyphosate

Currently, EPA 547 is the sole approved EPA method for determination of glyphosate and its MDL has not changed over time (Table 41). A voluntary consensus standard method (SM 6651) with similar determinative technology is also approved for use, but was used minimally over the duration of the selected studies according to PE records (Figure 25). The MDL of SM 6651 is not specified but in all likelihood, resembles the MDL of EPA 547. Therefore, the analytical methods capabilities for glyphosate determination have stayed constant for most laboratories. The available numerical WS data do not support a reassessment of the PQL based on the 75 percent criterion, because the passing rates of laboratories typically exceeded this value. In addition, the spike concentration of the WS samples were much higher than the current PQL.

Heptachlor

Results of the Method Comparison

The approved methods for the analysis of heptachlor, a Phase II SOC, in drinking water were listed in the NPDWRs (56 FR 3526). These original methods included gas chromatography with several extraction and/or detector variations (EPA Methods 505, 508, and 525.1). Since promulgation of the Phase II rule, EPA has removed one older method (EPA 525.1) and approved the use of three new analytical methods (EPA Methods 508.1, 525.2, and 551.1). As shown in Table 43, EPA Method 505 has experienced an estimated 10-fold increase in sensitivity. EPA Method 508.1 is nearly 7 times more sensitive than it was at the time of NPDWR promulgation, and represents the most sensitive of the new methods, with a current MDL of approximately 0.0015 µg/L. The MDLs of the newly approved methods, EPA Methods 508.1, 525.2, and 551.1, range from 0.5 to 15 times the MDLs of the most sensitive method at the time of the NPDWR promulgation.

Table 43. Results of the Analytical Methods Comparison for Heptachlor (Newly Promulgated Methods are Indicated in Bold)

MCL = 0.4 µg/L	**Current PQL = 0.4 µg/L**		**DL▲ = 0.04 µg/L**	**Acceptance Limit† = ± 45%**	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	GC, microextraction	0.03	EPA 505[2]	GC, microextraction	0.003
EPA 508[1]	GC, ECD	0.01	EPA 508[2]	GC, ECD	0.0015
EPA 525.1[1]	GC/MS, LSE	0.04	**EPA 508.1[2]**	GC, LSE, ECD	0.001 - 0.005*
			EPA 525.2[2]	GC/MS, LSE	0.059 - 0.15*
			EPA 551.1[2]	GC/MS, LLE, ECD	0.081

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

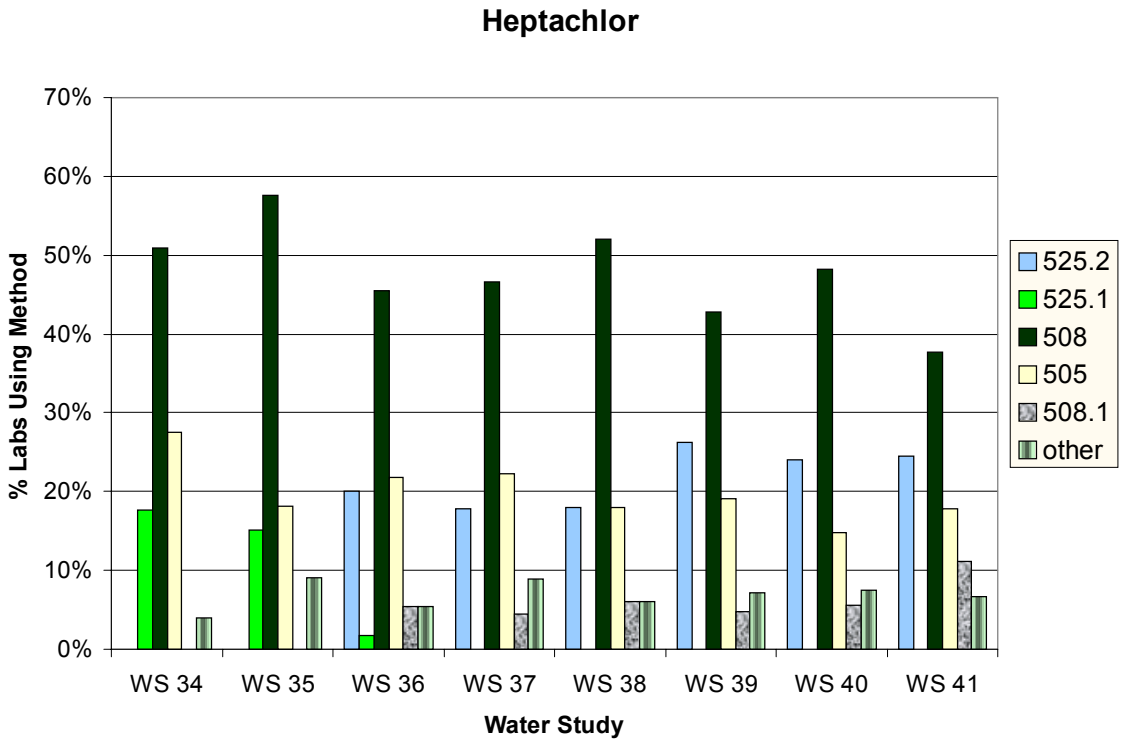
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 26 is a plot of the distribution of analytical techniques used by the EPA and State laboratories in WS 34 to 41. The "other" techniques represent methods which were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 26, the majority of laboratories used EPA 508 for determination of heptachlor in WS studies 34 to 41. EPA 525.1, which was used in earlier WS studies, was replaced by EPA 525.2 after WS 36. Other than this shift, there has been little overall change in method usage over time for this contaminant.

Figure 26. Distribution of Analytical Techniques by WS Study: Heptachlor



b. Results of the PQL Analysis

The original PQL for heptachlor (0.4 µg/L) was derived via multiplication of the IMDL by a factor of 10 (56 FR 3552). With the availability of recent PE WS data, efforts were made to reassess the PQL using data from WS studies 24 to 41. Table 44 summarizes the data from these WS studies, indicating the study number, the true value of the WS sample, the number of results from EPA and State laboratories, and the calculated percentage of laboratories whose results

successfully passed within federally designated acceptance limits for heptachlor. These acceptance limits are specified in 40 CFR §141.24(h)(19)(i) to be ± 45 percent from the true concentration of the spike sample.

The numerical data in Table 44 demonstrate that the laboratories in these WS studies are able to achieve results within the ± 45 percent acceptance window with 82 to 100 percent passing rates. Using the 75 percent criterion for estimation of the PQL, the dataset are not adequate to re-evaluate the PQL. Further, the majority of the spike samples had concentrations in excess of the current PQL of 0.4 µg/L. Nevertheless, the high passing rates of laboratories at concentrations around the PQL (e.g., 100 percent passing for a true value equal to 0.11 µg/L) support a possible reconsideration of the current PQL.

Table 44. Evaluation of Heptachlor Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
25b	0.113	18	100
24a	0.263	33	94
29	0.370	24	95.8
32	0.443	44	94.6
37	0.563	42	95.6
27	0.642	24	100
39	0.667	36	97.6
36	0.751	51	94.5
41	0.83	34	93
34	0.914	45	90.2
38	1.20	48	94
30	1.38	47	93.6
25a	1.42	19	100
31b	1.44	25	84.6
33	1.73	24	90.6
31a	1.92	27	81.5
26	2.27	31	90.3

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
40	2.33	50	90.7
35	2.54	30	90.9
24b	3.15	33	93.9

Conclusion for Heptachlor

The plot of the method usage over time (from WS studies) indicates consistent use of two methods, EPA Methods 508 and 505 over the duration of the selected studies, with laboratories slightly favoring usage of EPA 508. EPA 508 represents the most sensitive currently approved method, according to Table 43. The overall level of analytical sensitivity for this contaminant has improved approximately seven-fold from the time of NPDWR promulgation. The available numerical WS data do not support a reassessment of the PQL based on the 75 percent criterion, because the passing rates of laboratories always exceeded this value. Because such high passing rates were observed for some low spiked concentrations (e.g., 100 percent laboratory success for a concentration three times lower than the current PQL), it is possible that a lowered PQL might be appropriate. However, the desired quantitative reassessment of the PQL could not be performed using the historical approach.

Heptachlor Epoxide

Results of the Method Comparison

The approved methods designated in the Phase II rule for heptachlor epoxide (56 FR 3526) included EPA Methods 505, 508, and 525.1. These methods are variations of GC methods with different extraction and/or detection techniques as shown in Table 45. The most sensitive of the current methods is EPA 508.1 (GC with ECD), with an MDL of 0.001 µg/L. This method was introduced subsequent to the promulgation of the Phase II rule, along with two additional methods, EPA Methods 525.2 and 551.1.

Table 45. Results of the Analytical Methods Comparison for Heptachlor Epoxide (New Methods Indicated in Bold)

MCL = 0.2 µg/L Current PQL = 0.2 µg/L DL▲ = 0.02 µg/L Acceptance Limit† = ± 45%					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	GC, microextraction	0.004	EPA 505[2]	GC, microextraction	0.004
EPA 508[1]	GC, ECD	0.00015	EPA 508[2]	GC, ECD	0.0059
EPA 525.1[1]	GC/MS, LSE	0.2	**EPA 508.1[2]**	GC, LSE, ECD	0.001
			EPA 525.2[2]	GC/MS, LSE	0.048-0.13*
			EPA 551.1[2]	GC/MS, LLE, ECD	0.002

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR 141.24(h)(19)(i).

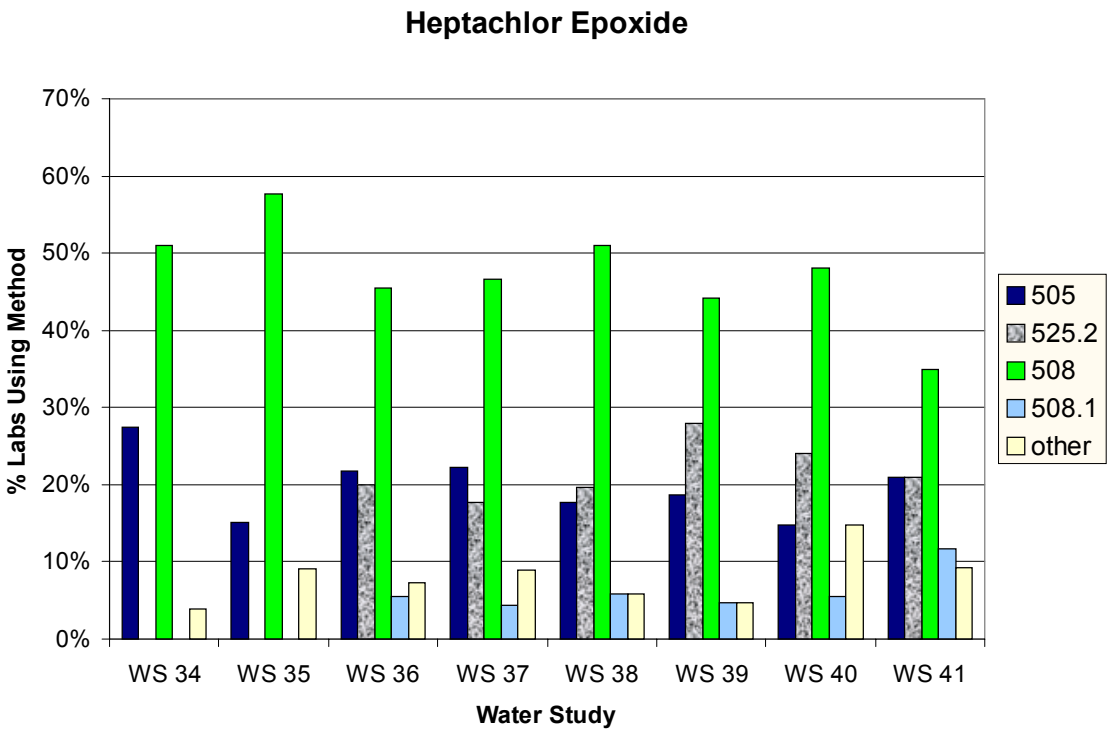
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 27 illustrates the distribution of the analytical techniques used by the EPA and State laboratories in WS 34 to 41. Analytical methods which were not reported by laboratories or were otherwise unknown were grouped into the category of "other." As illustrated by Figure 27, EPA 508 represents the most commonly used method for heptachlor epoxide WS analyses. EPA Methods 505 and 525.2 were used to a lesser degree; together, these methods account for 40 to 50 percent of the techniques used during the indicated time frame.

Figure 27. Distribution of Analytical Techniques by WS Study: Heptachlor Epoxide



b. Results of the PQL Analysis

The PQL for heptachlor epoxide is currently 0.2 µg/L. EPA obtained this value by multiplying the estimated IMDL by a factor of 10 (56 FR 3552). The Agency wished to re-evaluate the PQL using available WS data from WS studies 24 to 41 (although no data were available for WS 28). Table 46 summarizes these data, indicating the study number, the true value of the sample, the number of non-zero responses from laboratories, and the calculated passing rates of laboratories who satisfied the specified acceptance limits for heptachlor epoxide. These limits are designated as ± 45 percent (40 CFR §141.24(h)(19)(i)).

Table 46. Evaluation of Heptachlor Epoxide Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
24a	0.161	33	91
26a	0.198	31	87
29	0.267	25	92
39	0.340	43	98
32	0.346	55	95
37	0.403	45	93
27	0.533	24	88
34	0.55	51	94
41	0.63	43	95
33	0.679	31	94
38	0.742	51	96
25a	0.771	21	100
30	0.85	47	98
25b	0.094	20	100
40	1.48	54	94
35	1.49	33	97
24b	1.61	33	88
26b	1.81	30	97
31	1.92	27	82

The values in the last column of Table 46 demonstrate that the laboratories participating in these WS studies achieved a very high rate of success with respect to the designated acceptance limits. While the 75 percent criterion has historically been used to evaluate PQLs, such an analysis would be impossible for heptachlor epoxide because none of the laboratories exhibited success rates below this threshold. Thus, a regression of the WS results was not performed, as the data did not appear to contribute meaningfully to recalculate the PQL. In addition, the concentrations of the spike samples generally exceeded the concentration of interest, the PQL (0.2 µg/L).

Conclusion for Heptachlor Epoxide

According to the method comparison results, the introduction of three new analytical methods since the promulgation of the Phase II rule has not presented any significant improvements in overall method sensitivity. The most sensitive method (EPA 508) at the time of NPDWR promulgation is no longer the most sensitive method today, due to its MDL change, as evident in Table 45. Based on the analysis of method usage over time, EPA 508 is more widely used than the current most sensitive method, EPA 508.1. In light of the usage patterns for heptachlor epoxide, analytical method capabilities for the overall contaminant are probably similar to those of the original methods. Although the WS data did not provide enough information to perform a regression analysis, the passing rates at concentrations around the current PQL of 0.2 µg/L suggest that the PQL could be lower.

Hexachlorobenzene

Results of the Method Comparison

Hexachlorobenzene, a Phase V SOC, had three approved methods for drinking water analysis at the time NPDWRs were promulgated (57 FR 31776). All three original methods consisted of GC with extraction and/or detector variations (EPA 505, microextraction; EPA 508, ECD; and EPA 525.1, LSE). Since the Phase V rule was promulgated, the Agency has retained two of the old methods, removed EPA 525.1, and approved three additional analytical methods, EPA Methods 508.1, 525.2, and 551.1 (LSE, ECD; LSE; and LLE, ECD, respectively). As shown in Table 47, the most sensitive method of both the old and new categories is EPA 508, with an MDL of 0.0077 µg/L.

Table 47. Results of the Analytical Methods Comparison for Hexachlorobenzene (New Methods in Bold)

MCL = 1 µg/L	Current PQL = 1 µg/L		DL▲ = 0.1 µg/L	Acceptance Limit† = ± 2 x S.D.	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	GC, microextraction	0.002	EPA 505[2]	GC, microextraction	0.002
EPA 508[1]	GC, ECD	0.0077	EPA 508[2]	GC, ECD	0.0077
EPA 525.1[1]	GC/MS, LSE	0.2	**EPA 508.1[2]**	GC, LSE, ECD	0.001
			EPA 525.2[2]	GC/MS, LSE	0.001
			EPA 551.1[2]	GC/MS, LLE, ECD	0.001

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

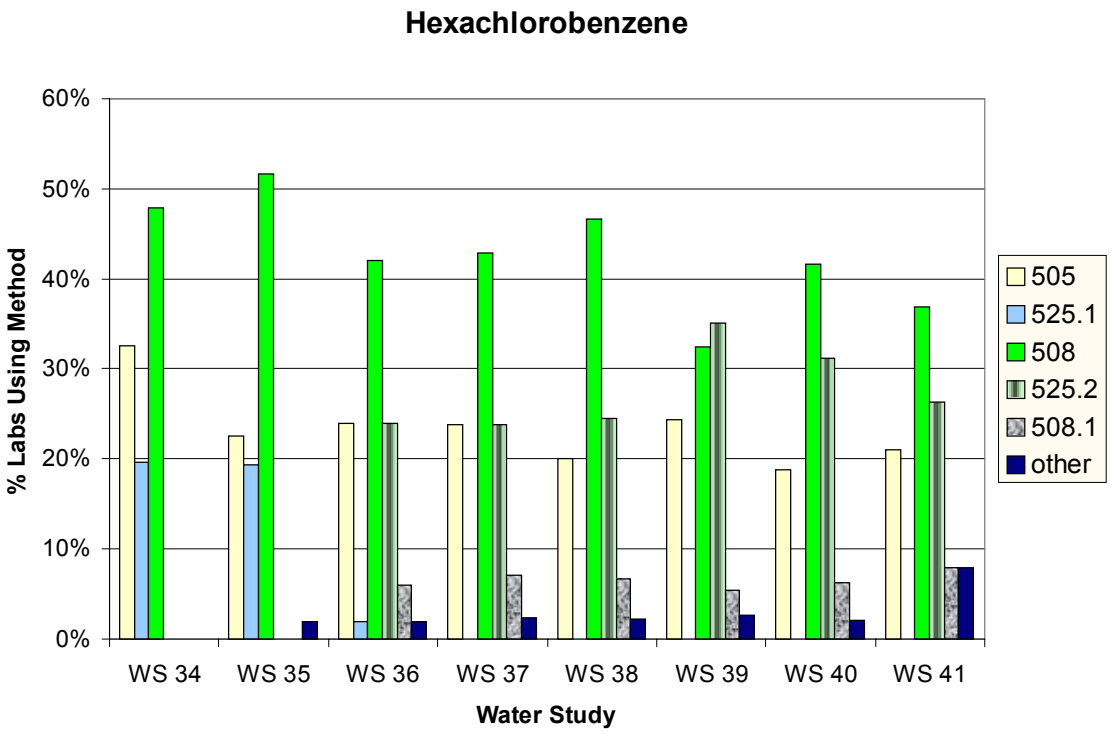
† Acceptance limits are listed at 40 CFR §141.24(h)(19)(i). S.D.=standard deviation.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the analytical techniques used by EPA and State laboratories in PE WS studies 34 to 41 is illustrated by Figure 28. Methods designated as "other" include methods for which laboratories did not specify the method used or were otherwise unknown. As shown by Figure 28, laboratories responding to these PE WS studies mainly determined hexachlorobenzene using EPA 508, with the exception of one study (WS 39) where use of EPA 525.2 was more prevalent. Use of EPA 525.2 began to appear in WS 36 and has increased slightly in recent years. The analytical methods used most recently (i.e., WS 41) for determination of hexachlorobenzene are divided between the several available current methods. Use of EPA 508.1 was quite small relative to the other methods used.

Figure 28. Distribution of Analytical Techniques by WS Study: Hexachlorobenzene



b. Results of the PQL analysis

The original PQL of hexachlorobenzene (1 µg/L, 56 FR 3552) was determined using PE data from WS 27. The data used for the re-evaluation of the PQL were taken from WS 27 through 41 (minus 28). The results of these WS studies are summarized in Table 48, which provides the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the results evaluated using acceptance limits of ± 2 x S.D (as specified at 141.24(h)(19)(i)).

It appears from the numerical data that EPA Regional and State laboratories are able to achieve successful results within the ± 2 x S.D. acceptance limits at rates well above the 75 percent criterion typically used for determining a PQL. Thus, a regression analysis using the available PE data was not attempted due to the nature of these data. On average, the success rates of the WS laboratories were about 92 percent over spike concentrations ranging from 0.4 to 3.6 µg/L. The high passing rates at concentrations around the PQL of 1 µg/L suggest that the PQL could be lower.

Table 48. Evaluation of PE Data for Hexachlorobenzene from WS Studies Using the 2 x S.D. Acceptance Limits (listed in order of increasing concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 2 x S.D. Acceptance Limits
29	0.417	18	83
27	0.483	15	100
38	0.538	45	93
35	0.635	31	90
30	0.667	38	95
37	0.806	42	95
36	0.847	50	88
32	0.857	44	89
41	1.03	38	97
33	1.32	29	93
39	1.68	37	97
31	2.4	23	87
40	2.9	48	92
34	3.57	46	89

Conclusion for Hexachlorobenzene

Together, the results from the method comparison and the method usage over time show that the most sensitive method, EPA 508, has been consistently used since the promulgation of the NPDWRs and is one of the more frequently used methods for determination of hexachlorobenzene. Thus, the MDL for the overall contaminant appears to be unchanged since the original methods were promulgated. Other less sensitive methods that are also currently in use include EPA Methods 505 and 525.2. Examination of the quantitative PE WS data reveal that the percentage of laboratories successfully passing the proficiency exams is too high to provide insight toward a re-evaluated PQL. However, the high laboratory passing rates at concentrations around the current PQL are suggestive of a change in the PQL.

Hexachlorocyclopentadiene

Results of the Method Comparison

With the promulgation of the NPDWRs for Phase V SOCs, the approved methodology for determination of hexachlorocyclopentadiene included two EPA gas chromatography methods, EPA 505 and 525.1. Since that time, EPA 525.1 was discontinued and four new methods were added (EPA Methods 525.2, 508.1, 551.1, and 508). As indicated in Table 49, the MDLs for the newer methods (EPA Methods 508.1 and 551.1) are lower than the MDLs of both original methods, while the MDLs of EPA Methods 505 and 525.2 are comparable to the MDL of the original EPA 505.

Table 49. Results of the Analytical Methods Comparison for Hexachlorocyclopentadiene

MCL = 50 µg/L	**Current PQL = 1 µg/L**	**DL▲ = 0.1 µg/L**	**Acceptance Limit† = ± 2*S.D.**		
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	Microextraction, GC	0.1	EPA 505[2]	Microextraction, GC	0.13
EPA 525.1[1]	LSE, GC/MS	0.03	**EPA 525.2[2]**	LSE, GC/MS	0.1
			EPA 508.1[2]	LSE, GC with ECD	0.004
			EPA 551.1[2]	LLE, GC with ECD	0.018
			EPA 508[2]	GC with ECD	N/A◇

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at 40 CFR §141.24(h)(19)(i).

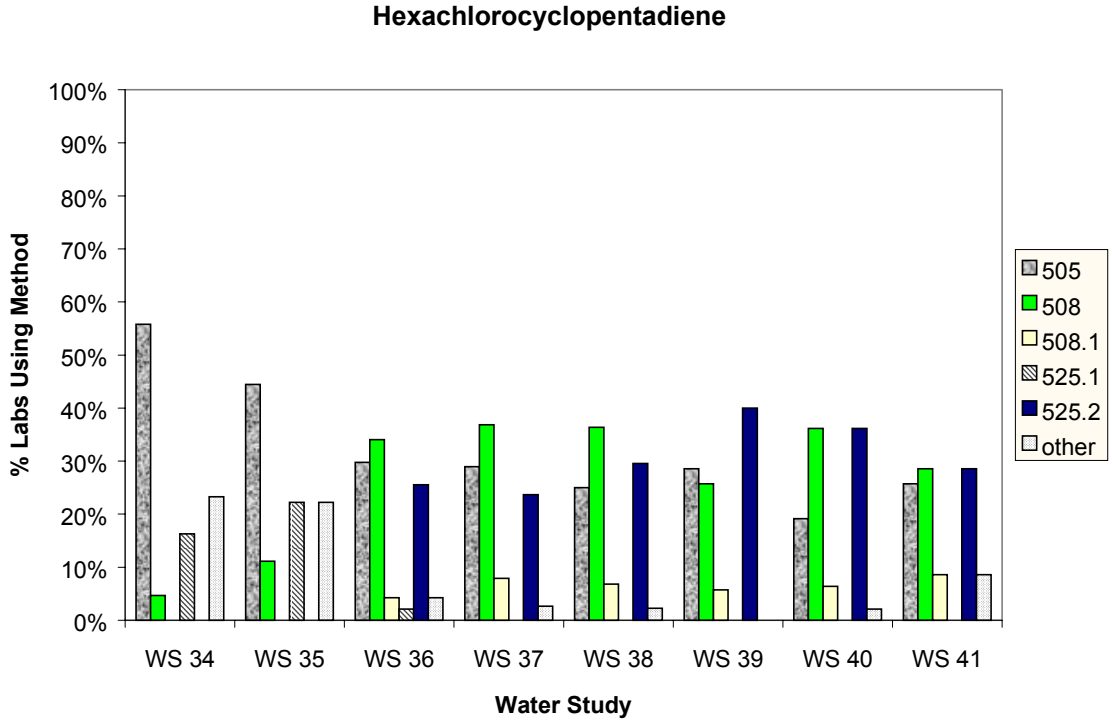
◇ N/A = not available.

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 29 illustrates the distribution of the analytical techniques used by EPA and State laboratories in WS studies 34 to 41. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as methods for which laboratories did not report any information on the type of method used. The distribution of methods used by EPA and State laboratories has been fairly well-mixed. During WS 34 and 35, EPA 505 was the predominant choice for determination of hexachlorocyclopentadiene. From WS 36 to 41, however, use of EPA Methods 508 and 525.2 began to eclipse that of EPA 505. The remaining methods were used minimally throughout WS 34 to 41.

Figure 29. Distribution of Analytical Techniques by WS Study: Hexachlorocyclopentadiene



b. Results of the PQL Analysis

The current PQL of 1.0 µg/L was originally set from PE data from WS 23 through 27 (57 FR 31801). The PQL re-evaluation used data from WS 24 to 41 (with the exception of WS 28 which had no available data). Table 50 summarizes the results of these studies, providing the study

number, the spiked value for the WS sample, the number of results from EPA Regional and State laboratories, and the passing rates of these laboratories when evaluated using an acceptance limit of ± twice the standard deviation (as specified at 141.24(h)(19)(i)).

Table 50. Evaluation of Hexachlorocyclopentadiene Data from WS Studies Using the ± 2* S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 2* S.D. Acceptance Limits
25b	0.267	11	54.5
29	0.313	14	92.9
26b	0.367	21	95.2
24b	0.736	21	95.2
27	0.774	14	100
32	0.823	41	87.8
31	1.11	16	93.8
40	1.22	47	93.6
38	1.47	44	93.2
30	1.72	35	100
35	1.84	27	92.6
25a	1.87	12	83.3
41	1.93	35	97.1
34	2.14	43	95.3
26a	2.47	21	81.0
37	2.49	40	95.0
33	2.92	26	96.2
39	3.26	35	94.3
24a	4.42	21	90.5
36	4.71	47	93.6

As shown in Table 50, laboratories exhibited passing rates over 75 percent in all WS studies with the exception of one (WS 25b). Because the passing rates for laboratories determining hexachloropentadiene were well above 75 percent, a re-evaluation of the PQL was not feasible. However, the demonstrated success of laboratories at concentrations well below the existing PQL of 1 µg/L (e.g., WS 27, 29 and 32) suggests that a lower PQL may be possible.

Conclusion for Hexachlorocyclopentadiene

The method comparison results indicate that method sensitivities have either remained similar or improved slightly (e.g., for EPA Methods 508.1 and 551.1). A review of method usage over time shows that EPA Methods 505, 525.2, and 508 were the most commonly used methods in recent WS studies. Because the more sensitive methods were not used with great frequency, it would appear that method capabilities for hexachlorocyclopentadiene have remained more or less unchanged over time. Although it was not possible to recalculate the PQL, high laboratory passing rates at concentrations below the current PQL suggest that a lower PQL may be feasible.

Mercury

Results of the Method Comparison

The analytical methods approved for the determination of mercury under the NPDWRs for Phase II IOCs include EPA Methods 245.1 and 245.2 (56 FR 3526). Since the time of promulgation, EPA Method 200.8 has been approved. The currently approved methods for mercury determination include EPA Methods 200.8, 245.1, and 245.2. Table 51 summarizes the MDLs for both the original and current approved versions of the methods. As shown in Table 51, the MDLs for current methods are equal in sensitivity to past methods.

Table 51. Results of the Analytical Methods Comparison for Mercury (Newly Promulgated Methods Indicated in Bold)

MCL = 2 µg/L Current PQL = 0.5 µg/L DL‸ = 0.2 µg/L Acceptance Limit† = ± 30%					
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 245.1[1]	Manual, Cold Vapor	0.2	**EPA 200.8[2]**	ICP-MS	0.2
EPA 245.2[1]	Automated, Cold Vapor	0.2	EPA 245.1[1]	Manual, Cold Vapor	0.2
			EPA 245.2[1]	Automated, Cold Vapor	0.2

[1] "Methods for Chemical Analysis of Water and Wastes," EPA/600/4-79/020, March 1983.

[2] "Methods for the Determination of Metals in Environmental Samples–Supplement I," EPA/600/R-94/111, May 1994.

‸ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.23(a)(4)(i) and depend on analytical method.

† Acceptance limits are listed at 40 CFR §141.23(k)(3)(ii) for inorganic compounds.

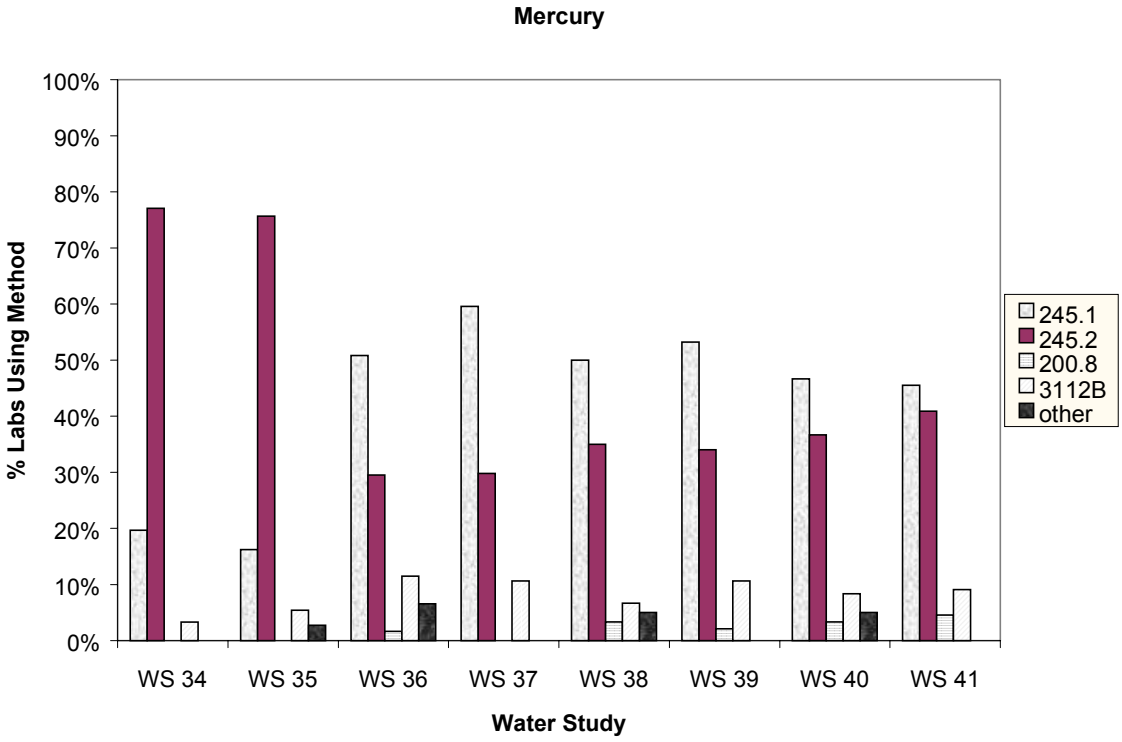
Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 30 shows the distribution of analytical techniques used by EPA and State laboratories for WS studies 34 to 41. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as "unknown" methods, (i.e., methods for which laboratories did not report any information on the type of method used).

As shown in Figure 30, EPA Method 245.2 (automated cold vapor) was the most widely used method in WS 34 and 35. From WS 36 to WS 41, EPA Methods 245.1 (manual cold vapor) and 245.2 were most commonly used.

Figure 30. Distribution of Analytical Techniques by WS Study: Mercury



b. Results of the PQL Analysis

The current PQL of 0.5 µg/L was originally set using previous PE data (56 FR 3549). With the availability of more current data from WS 24 to 41, a PQL re-evaluation was attempted. Table 52 summarizes the results of these water studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the mercury results evaluated using an acceptance limit of ± 30 percent, as designated in 40 CFR § 141.23(k)(3)(ii).

Table 52. Evaluation of Mercury Data from WS Studies Using the 30% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 30% Acceptance Limits
29	0.506	31	87.1
25a	0.720	37	70.3
35	0.897	37	94.6
31	0.908	31	87.1
27	1.29	33	97.0
40	1.50	60	93.3
33	1.77	34	94.1
24b	2.16	59	94.9
26b	2.47	61	93.4
36	3.00	61	95.1
30	3.46	62	100.0
39	3.80	47	83.0
25b	4.32	37	91.9
26a	4.56	61	96.7
34	5.09	61	100.0
24a	5.76	59	96.9
41	5.82	44	100.0
32	6.23	64	96.9
38	6.39	60	95.0
37	8.16	47	91.5

The data from the available WS studies were not conducive to recalculation of the PQL because the percentage of labs passing (with the exception of one study) generally exceeded the standard 75 percent passing criterion needed to evaluate the PQL using the either a linear regression or graphical approach. In addition, the majority of the true values were above the original PQL of 0.5 µg/L. However, at values slightly above the current PQL (e.g., WS 29 and

25a) the passing rates of 87 and 70 percent would indicate that the current PQL is most likely in the appropriate range.

Conclusion for Mercury

Since the promulgation of the NPDWR for mercury, EPA 200.8 has been added to the original two analytical methods approved for the measurement of mercury in drinking water (EPA 245.1 and 245.2). The three methods currently approved for mercury are all equal in sensitivity with an MDL of 0.2 µg/L. According to the distribution of analytical methods usage over time, EPA 245.2 was more widely used than EPA 245.1 during WS 34 to 35. From WS 36 to 41, these two methods were utilized with approximately the same frequency. Upon review of the WS data, a high percentage of laboratories successfully passing the WS studies prevented a recalculation of the PQL at the 75 percent passing rate. Thus, the available PE data provided little evidence for a lower PQL using this approach. Observation of laboratory passing rates at concentrations slightly above the current PQL of 0.5 µg/L suggests that this PQL is still in all likelihood appropriate.

Methoxychlor

Results of the Method Comparison

At the promulgation of the NPDWRs for methoxychlor, three methods were approved for the determination of this compound: EPA Methods 505, 508, and 525.1 (56 FR 3552). Since that time, use of EPA 525.1 has been discontinued and additional methods have been approved, including EPA Methods 508.1, 525.2, and 551.1. All approved methods utilize GC in various forms. As shown in Table 53, the MDL of EPA 505 has changed little over time, whereas the MDL of EPA 508 has improved in sensitivity. The MDLs of the newer methods (in bold) range from 0.008 to 0.1 µg/L. The most sensitive method currently available (EPA 551) has about 125 times the sensitivity of the original EPA 505.

Table 53. Results of the Analytical Methods Comparison for Methoxychlor (Newly Promulgated Methods in Bold)

MCL = 40 µg/L	Current PQL = 10 µg/L		DL‘ = 0.1 µg/L	Acceptance Limit† = ± 45%	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	Microextraction, GC	1.0	EPA 505[2]	Microextraction, GC	0.96
EPA 508[1]	GC with ECD	0.05	EPA 508[2]	GC with ECD	0.022
EPA 525.1[1]	GC/MS with LSE	40	**EPA 508.1[2]**	GC with LSE, ECD	0.015
			EPA 525.2[2]	GC/MS with LSE	0.1
			EPA 551.1[2]	GC with LLE, ECD	0.008

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

‘ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(h)(18).

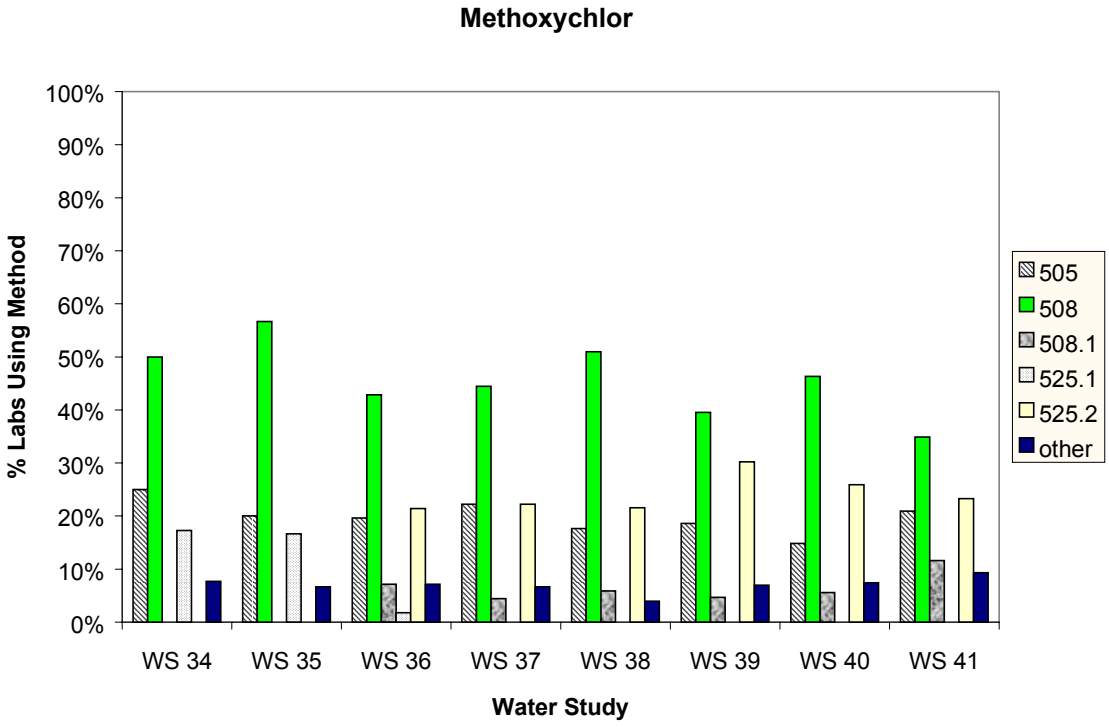
† Acceptance limits for organic compounds are listed at 40 CFR § 141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of methods used by EPA and State laboratories participating in WS 34 to 41 is depicted in Figure 31. The category of "other" includes any unidentified techniques used by participating laboratories. As Figure 31 shows, EPA 508 was used most widely by participating laboratories during WS 34 to 41. As EPA 525.1 was phased out in WS 36, use of newer methods, EPA Methods 525.2 and 508.1, began. EPA 505 and other unidentified methods were used intermittently throughout WS 34 to 41.

Figure 31. Distribution of Analytical Techniques by WS Study: Methoxychlor



b. Results of the PQL Analysis

The PQL for methoxychlor was originally proposed at 0.001 mg/L, but was finalized in 1991 at 0.01 mg/L (or 10 µg/L). The method for deriving this value was multiplication of the detection limit by a factor of ten (56 FR 3551). Recently, with the availability of more recent laboratory performance data from WS 24 to 41, a reassessment of the existing PQL was conducted. Table 54 summarizes each WS result including the spiked (or "true") concentration in the test sample, the number of participating laboratories, and the calculated percentage of laboratories successfully passing within the specified ± 45 percent acceptance limit for methoxychlor (141.24(h)(19)(i)).

Table 54. Evaluation of Methoxychlor Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
26b	2.18	59	98.3
25a	3.17	37	94.6
29	5.21	33	97.0

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
24b	5.37	61	93.4
31	12.9	32	81.3
34	14.2	52	92.3
27	16.6	39	89.7
32	17.4	59	88.1
37	18.5	45	93.3
41	26.8	43	90.7
36	28.9	56	92.9
30	34.2	54	88.9
38	34.8	51	88.2
33	42.3	35	97.1
40	42.8	54	96.3
25b	48.8	37	94.6
39	53.8	43	93.0
35	62.6	30	96.7
24a	73.2	62	91.9
26a	92.8	59	93.2

Table 54 reveals that the percentage of passing laboratories was well above the 75 percent criterion, and thus, the PQL could not be re-evaluated using the regression technique. Table 53 also shows that even at very low concentrations (e.g., one-fifth of the existing PQL), a large percentage of EPA and State laboratories was able to pass the WS study, suggesting that a lower PQL may be feasible.

Conclusion for Methoxychlor

EPA Methods 505, 508, and 525.1 were originally approved for the determination of methoxychlor with the promulgation of the NPDWRs for Phase II SOCs in 1991. Since then, EPA 525.1 has been removed while EPA Methods 508.1, 525.2, and 551.1 have been added to the approved list. A review of the method usage over time shows that laboratories participating in WS 34 to 41 utilized EPA 508 more frequently than all other approved methods, although this margin of difference began to decrease in more recent WS studies. A revised PQL for

methoxychlor could not be determined due to the large percentage of laboratories surpassing the 75 percent criterion. However, the data do reveal a possible basis for lowering the PQL based on the high success rates of laboratories at concentrations well below the current PQL.

Oxamyl

Results of the Method Comparison

Oxamyl is one of several SOCs first regulated under the Phase V Rule (57 FR 31776). Under this rule, EPA 531.1 (a HPLC method) was approved for determination of oxamyl. More recently, the Agency has approved an additional analytical method, Standard Method (SM) 6610 (HPLC followed by post-column reaction and fluorescence detection), while retaining the use of EPA 531.1. The MDL for SM 6610 is not specified, as methods published by organizations outside the Agency are not required to calculate an MDL. The MDL for EPA 531.1 has not changed since the 1988 Phase V Rule promulgation, signifying no change in analytical sensitivity for this contaminant.

Table 55. Results of the Analytical Methods Comparison for Oxamyl

MCL = 200 µg/L Current PQL = 20 µg/L DL▲ = 2 µg/L Acceptance Limit† = ± 2*S.D.					
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 531.1[1]	HPLC	2.0	EPA 531.1[2]	HPLC	2.0
			SM 6610[3]	HPLC-post column reaction/ fluorescence detection	NA*

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

[3] Standard Method 6610. Supplement to the 18th edition of Standard Methods for the Examination of Water and Wastewater, 1994, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

▲ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits are listed at 40 CFR §141.24(h)(19)(i).

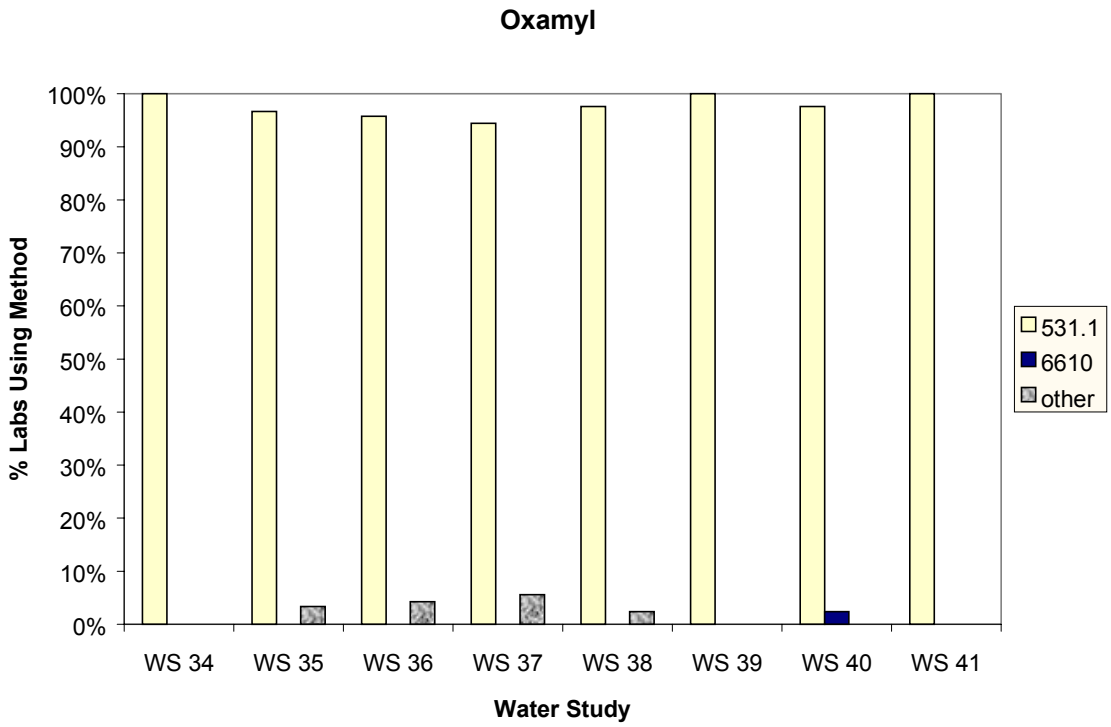
* MDLs not provided for voluntary consensus standard methods.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the methods used by EPA Regional and State laboratories in WS studies 34 to 41 is shown in Figure 32. The results for "other" techniques in this figure include methods for which laboratories did not report any information on the type of method used or reported codes that could not be identified. As shown in Figure 32, EPA 531.1 was the most widely used analytical method for determination of oxamyl during WS 34 to 41. By contrast, the more recently approved SM 6610 was only used minimally during WS 40.

Figure 32. Distribution of Analytical Techniques by WS Study: Oxamyl



b. Results of the PQL Analysis

The current PQL of 20 µg/L was originally determined using a ten times MDL multiplier (56 FR 30370). In re-evaluating the PQL, a broader range of PE data from WS 24 to 41 were analyzed. Table 56 summarizes the results of these water studies, providing the study number, the spiked (or "true") value for the WS sample, the number of results from EPA and State laboratories, and the percentage of laboratories that successfully passed the test using an acceptance limit of $\pm$ 2*S.D. (specified at 141.24(h)(19)(i)).

Table 56. Evaluation of Oxamyl Data from WS Studies Using the ± 2* S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA Regional and State Labs	% Labs Passing ± 2* S.D. Acceptance Limits
29	4.60	10	10.0
31	5.72	14	0.00
30	6.47	25	24.0
27	12.4	8	25.0
24a	12.5	8	75.0
32	12.8	36	50.0
25a	17.6	5	60.0
34	22.5	43	76.7
26a	22.6	13	76.9
33	26.2	13	46.2
24b	31.3	8	87.5
41	33.8	29	86.2
36	34.1	47	80.9
40	42.7	42	95.2
37	46.4	36	83.3
26b	46.4	13	76.9
35	47.2	30	83.3
25b	53.5	5	80.0
38	58.8	42	90.5
39	78.7	32	90.6

The WS data for the EPA Regional and State laboratories shown in Table 56 were also used to develop a linear regression. The spiked value concentration is the independent variable (x) and the percentage of laboratories achieving acceptable results (within the acceptance window) is the dependent variable (y). For the equation $y = mx + b$, m stands for the slope of the regression line (change in the percentage of laboratories passing as spiked concentration increases) and b stands for the y-intercept.

The use of regression techniques assumes that the data from the various WS studies form a single continuous data set. In reality, the study results do not form a continuous data set, but represent results from samples spiked at specific discrete concentrations of oxamyl and analyzed a few at a time over an extended period. However, through the use of a linear regression, the data can be used to create a model (the regression line) that may be useful in predicting accuracy and precision as a function of the concentration of the samples. The regression determines the linear relationship that best fits the observed results, in effect smoothing the curve and ensuring that there is a unique concentration that corresponds to any percentage of acceptable laboratories.

Calculating the regression equations also provides the correlation coefficient (r) for the regression, which is a measure of the degree to which the actual data fit the linear model represented by the regression line. An r value of one would indicate a perfect fit with a positive slope of the data to the model. A value, p, can also be calculated for the regression that indicates the probability of concluding the null hypothesis (in this case that the spiked value concentration is linearly correlated with the percentage of labs achieving acceptable results) is false, when in fact the null hypothesis is true, for the given data set. In statistical terms, p indicates the probability of a Type I error. The results for the regression equation are summarized in Table 57.

Table 57. Regression Results for Oxamyl

Regression Term	±2*S.D. Acceptance Limits
m	0.0125
b	0.223
r	0.819
p	0.005

The r value of 0.82 indicates that the data fit the linear model fairly well. The p value of 0.005 indicates that the spiked value and the percentage acceptable are linearly correlated with more than 99 percent confidence.

Figure 33 shows the graphical results of the regression. The observed data were plotted against the WS spiked value concentration and the results predicted from the linear regression line were superimposed. The observed success rate for the EPA and State laboratories is noticeably lower than the predicted success rate in the region below 20 µg/L. While attempts might be made to model the observed results using a second order (non-linear) regression, the Agency does not believe that there is a scientifically valid reason to do so. Figure 34 also shows that the percentage of laboratories achieving acceptable results reaches 75 percent at a concentration of 39.5 µg/L which, by the graphical method, indicates the value of the re-evaluated PQL (RPQL). This concentration is higher than the existing PQL of 20 µg/L.

The oxamyl PE data illustrate the expected outcome from PE testing: a lower percentage of labs passing at the lowest true values, with an increasing percentage of labs passing as true values increase, due to increasing lab analytical capabilities at higher concentrations. As true values increase further, the percentage of labs passing approaches a stable plateau beyond which lab analytical capabilities do not improve. This results in a two-part distribution: the lower true values (<30 µg/L) are characterized by a line of steeper slope, while higher true values (>30 µg/L), are characterized by a line that is nearly flat (see Figure 33). Using this graph to visually estimate a re-evaluated PQL, the original choice of 20 µg/L appears to be appropriate.

Figure 33. PQL Evaluation of PE WS Data: Oxamyl

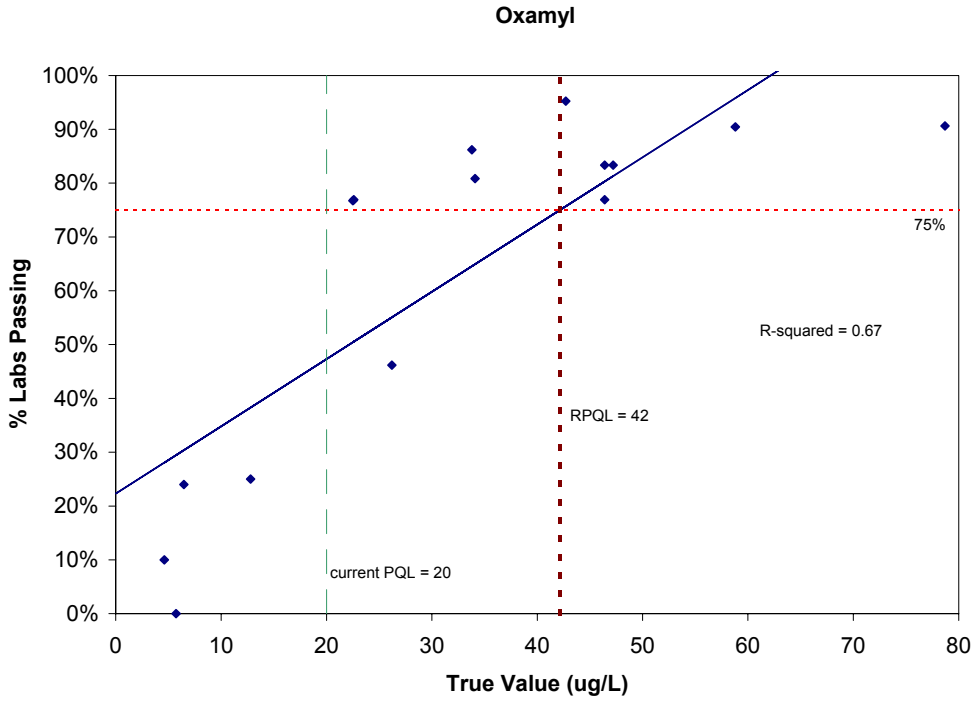
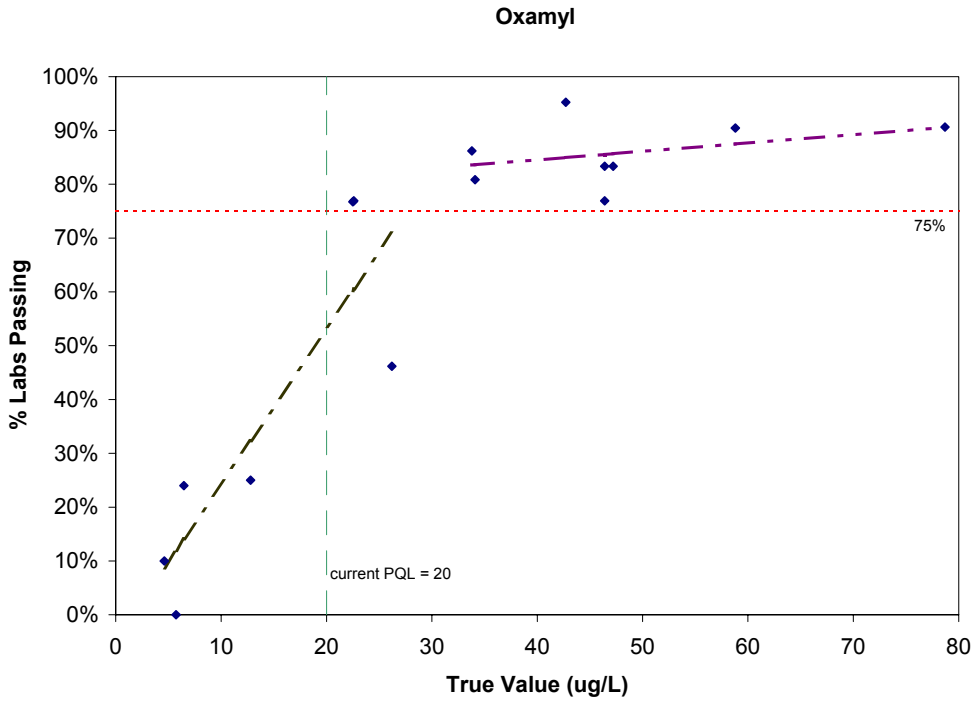


Figure 34. Two-part Distribution of Oxamyl WS Data



Conclusion for Oxamyl

Although a new method for the determination of oxamyl was introduced (SM 6610), this method was rarely used, as seen in the graph of method usage over time (Figure 32). Due to the overwhelming continued usage of EPA 531.1, whose MDL has not changed, analytical methods capabilities appear to have remained unaltered over time. Based on the PQL reassessment, it is apparent that laboratory success follows a linear relationship with true value concentration to a point, after which the success rate plateaus. Using the standard linear regression approach, the new RPQL was determined to be 39.5 µg/L, which may be linked to higher spiked concentrations exhibited in more recent PE WS data. However, if the data are not plotted on a single line but rather in the two-part manner of Figure 34, the RPQL would most likely resemble the existing value of 20 µg/L. It is likely that the PQL may lie somewhere between 20 and 40 µg/L.

PCBs

Results of the Method Comparison

For the NPDWRs, all polychlorinated biphenyls (PCBs) were collectively grouped and identified by the particular aroclor decachlorobiphenyl (DCBP). In 1991, EPA approved EPA

508A for determination of DCBP, a Phase II SOC (56 FR 3526), in drinking water. This analytical method utilizes gas chromatography with perchlorination. Since promulgation of the Phase II rule, EPA has not changed the status of EPA 508A and its MDL remains at 0.1 µg/L (Table 58).

Table 58. Results of the Analytical Methods Comparison for PCBs (Newly Promulgated Methods are Indicated in Bold)

MCL = 0.5 µg/L	**Current PQL = 0.5 µg/L**		**DL▲ = 0.1 µg/L**	**Acceptance Limit† = ± 100%**	
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 508A[1]	Perchlorination with GC	0.1	EPA 508A[1]	Perchlorination with GC	0.1

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Because only one method, EPA 508A, was approved for determination of PCBs (as DCBP) over the duration of WS 34 to 41, its usage was not plotted.

b. Results of the PQL Analysis

The original PQL for PCBs was proposed at five times the MDL of 0.1 µg/L. For the final rule, EPA compared this value with multilaboratory performance data from WS studies 22 to 24, and found the PE data to support the proposed value, 0.5 µg/L (56 FR 3552). For the six-year regulatory review, new efforts have been made to reassess the PQL using more recent PE WS data from WS 31 to 41. These data are summarized in Table 59, which indicates the study number, the true value of the WS sample, the number of results returned by EPA and State laboratories, and the calculated percentage of laboratories whose results successfully passed within designated acceptance limits for PCBs (±100 percent, as specified at 40 CFR §141.24(h)(19)(i)).

Table 59. Evaluation of PCBs Data from WS Studies Using the ± 100% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 100% Acceptance Limits
31	0.445	13	69.2
37	0.527	27	92.6
35	0.596	15	80.0
39	0.667	26	96.2
38	0.733	27	92.6
33	0.807	14	92.9
32	0.959	22	95.5
34	1.08	26	96.2
36	1.13	30	93.3
40	1.23	27	100
41	1.80	21	100

A PQL is historically derived from a concentration at which 75 percent of the participating laboratories pass, or report concentrations that fall within the specified acceptance limits. However, the data in Table 59 indicate that laboratories exceeded the required 75 percent criterion in almost all studies (with the exception of WS 31). Because of the high laboratory passing rates and a lack of sufficient spike concentrations below 0.5 µg/L, the PQL for PCBs could not be re-evaluated graphically with these data. However, the two of the three lowest spike concentrations close to the current PQL, WS 31 (0.445 µg/L) and WS 35 (0.596 µg/L), had passing rates of 69 and 80 percent, respectively. These passing rates suggest that the current PQL of 0.5 µg/L is unlikely to change.

Conclusion for PCBs

Since the promulgation of the NPDWR for PCBs, EPA 508A has been the only method approved for PCB determination. As the current PQL was derived from the MDL multiplier method rather than multi-laboratory performance data, a PQL re-evaluation was attempted using current PE data from WS 31 to 41. The high percentage of laboratories passing the PE testing within the designated acceptance limits and the relatively high spike concentrations prevented a conclusive re-evaluation of the PQL using the historical approach. However, spike concentrations close to the current PQL had laboratory passing rates close to 75 percent. This suggests that the current PQL is appropriate and unlikely to change.

Pentachlorophenol

Results of the Method Comparison

With the promulgation of NPDWRs for Phase II SOCs, two methods were approved for the determination of pentachlorophenol in drinking water: EPA Methods 515.1 and 525.1 (56 FR 3526). Since promulgation of this rule, EPA removed EPA 525.1 and approved the use of five new or updated methods: EPA Methods 515.2, 515.3, 555, 525.2, and ASTM Method D5317-93 (GC with ECD), a voluntary consensus method. The MDLs of these methods are indicated in Table 60.

Table 60. Results of the Analytical Methods Comparison for Pentachlorophenol (Newly Promulgated Methods Are Indicated in Bold)

MCL = 1 µg/L Current PQL = 1 µg/L DL▲ = 0.04 µg/L Acceptance Limit† = ± 50%					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 515.1[1]	GC with ECD	0.076	EPA 515.1[2]	GC with ECD	0.032
EPA 525.1[1]	LSE, GC/MS	0.3 - 3.0*	**EPA 525.2**[2]	LSE GC/MS	0.72 - 0.1*
			EPA 515.2[3]	LSE, GC with ECD	0.16
			EPA 555[3]	LLE, derivatization and GC with ECD	0.15 - 1.6*
			EPA 515.3[4]	LLE, derivatization and GC with ECD	0.021 - 0.085*
			D5317-93[5]	GC with ECD	N/A◇

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

[3] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement II," EPA/600/R-92/129, August 1992.

[4] "Determination of Chlorinated Acids in Drinking Water by Liquid-liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection," Revision 1.0, EPA/815/B-99/001, July 1996.

[5] *Annual Book of ASTM Standards*, Vol. 11.01. American Society for Testing and Materials, 1961 Race Street. Philadelphia, PA 19103.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

* Multiple MDL values result from variability of reagents, instrumentation and/or laboratory performance.

◊ N/A = not available. MDLs for voluntary consensus standard methods are not specified.

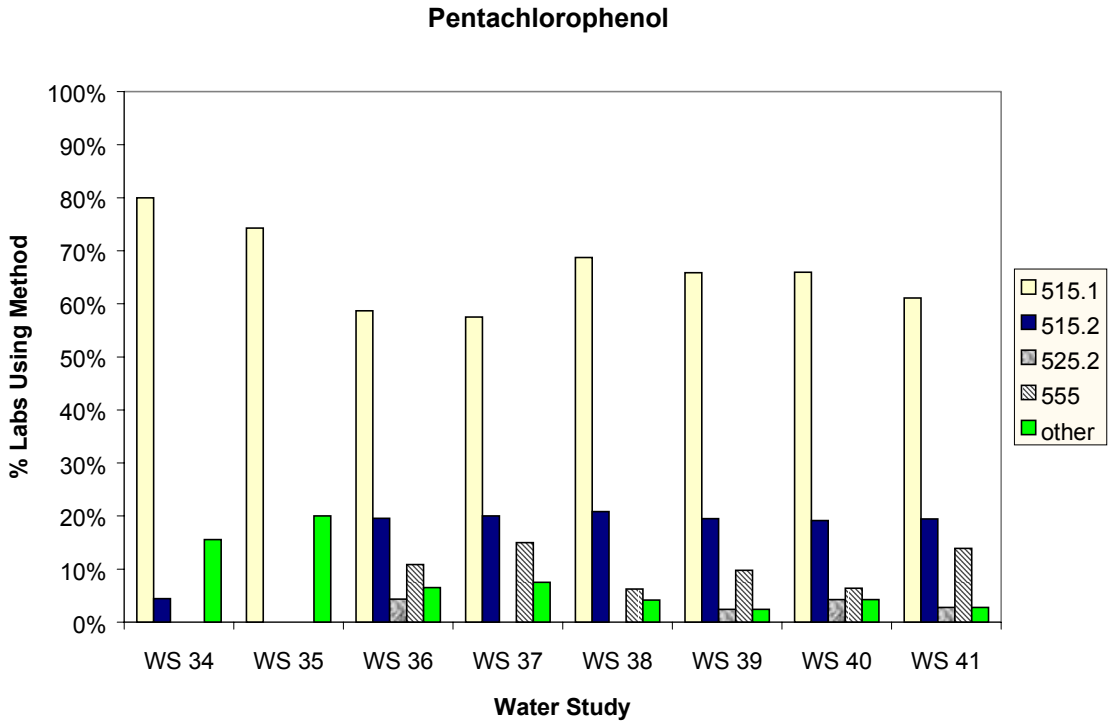
As shown in Table 60, most of the current EPA methods for pentachlorophenol do not display a significant increase in analytical sensitivities as compared to the methods approved at the time of the Phase II rule promulgation. The exception is EPA 515.1, which has approximately twice the sensitivity of the prior version of the same method approved at the time of promulgation.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of analytical methods used by the EPA and State laboratories in WS 34 to 41 is plotted in Figure 35. The "other" techniques represent methods which were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 35, despite the addition of several new analytical methods, the majority of laboratories still favored the use of EPA 515.1 for determination of pentachlorophenol during WS 34 to 41. The more recently approved EPA Methods 515.2 and 555 were used much less frequently, by comparison. EPA 525.2 was only used intermittently during the study period.

Figure 35. Distribution of Analytical Techniques by WS Study: Pentachlorophenol



b. Results of the PQL Analysis

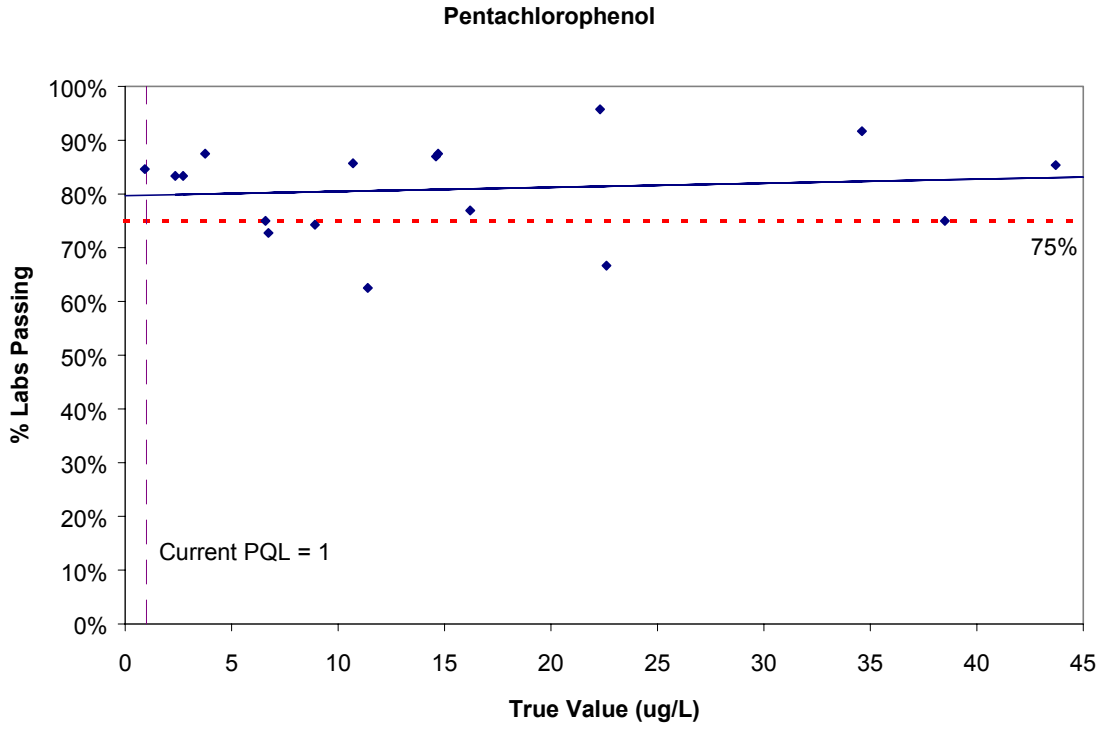
EPA determined the current PQL of 1 µg/L (0.001 mg/L) for pentachlorophenol using earlier water supply data (WS 22 to 25, 56 FR 3552). A re-evaluation of the PQL was attempted using more recent PE data from WS 24 to 41. Table 61 summarizes the data from these WS studies (with the exception of WS 25, 27, 28, and 30), indicating the study number, the true value of the WS sample, the number of results from EPA and State laboratories, and the percentage of laboratories whose results successfully passed the acceptance limits of ± 50 percent for pentachlorophenol (40 CFR §141.24(h)(19)(i)).

Table 61. Evaluation of Pentachlorophenol Data from WS Studies Using the ± 50% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 50% Acceptance Limits
24a	0.924	13	84.6
33	2.72	24	83.3
26a	3.75	16	87.5
37	6.59	40	75.0
29	6.73	11	72.7
35	8.91	35	74.3
32	10.7	35	85.7
31	11.4	16	62.5
36	14.6	46	87.0
38	14.7	48	87.5
24b	16.2	13	76.9
40	22.3	47	95.7
34	22.6	45	66.7
41	34.6	36	91.7
26b	38.5	16	75.0
39	43.7	41	85.4

Visual examination of the data show that with the exception of three WS studies (WS 29, 35 and 34), the laboratory passing rates exceeded the 75 percent criterion and only one WS study had a spike concentration below the current PQL of 1 µg/L. Because many of the laboratories achieved high success rates during PE testing for pentachlorophenol, the resulting regression line, shown in Figure 36, failed to intersect the 75 percent line that would have indicated the new estimated PQL. Furthermore, there were very few water studies with spiked samples below the current PQL. Thus, a new PQL could not be derived using this procedure.

Figure 36. Evaluation of PE WS Data: Pentachlorophenol



Conclusion for Pentachlorophenol

The plot of the method usage over time for WS 34 to 41 indicates laboratories consistently used EPA 515.1 more frequently than other methods. The detection limit for EPA 515.1 has not changed over time, as shown by the results of the method comparison (Table 60). The available WS data did not provide a basis for lowering the PQL for two reasons: the passing rates of laboratories were generally greater than the 75 percent criterion for PQL estimation and the true value concentrations typically exceeded the current PQL.

Picloram

Results of the Method Comparison

Picloram became a regulated SDWA contaminant in 1992 with the promulgation of NPDWRs for Phase V SOCs (57 FR 31776). At that time, the sole method approved for determination of picloram in drinking water was EPA 515.1. Since promulgation of the Phase V rule, EPA has added two methods to the approved list: EPA Methods 515.2 and 555. Table 62

summarizes MDL information for the current and former approved methods for picloram. EPA 555 is about five times less sensitive compared to earlier methods.

Table 62. Results of the Analytical Methods Comparison for Picloram (Newly Promulgated Methods Are Indicated in Bold)

MCL = 500 µg/L	Current PQL = 1 µg/L	DL▲ = 0.1 µg/L	Acceptance Limit† = 2*S.D.		
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 515.1[1]	GC with ECD	0.1	EPA 515.1[2]	GC with ECD	0.14 (EDL)◊
			EPA 555[2]	HPLC with a Photodiode Array Ultraviolet Detector	0.5
			EPA 515.2[3]	LSE, GC with ECD	0.35

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water Supplement II," EPA/600/R-92/129, August 1992.

[3] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(h)(18).

† Acceptance limits for organic compounds are listed at are listed at 40 CFR §141.24(h)(19)(i).

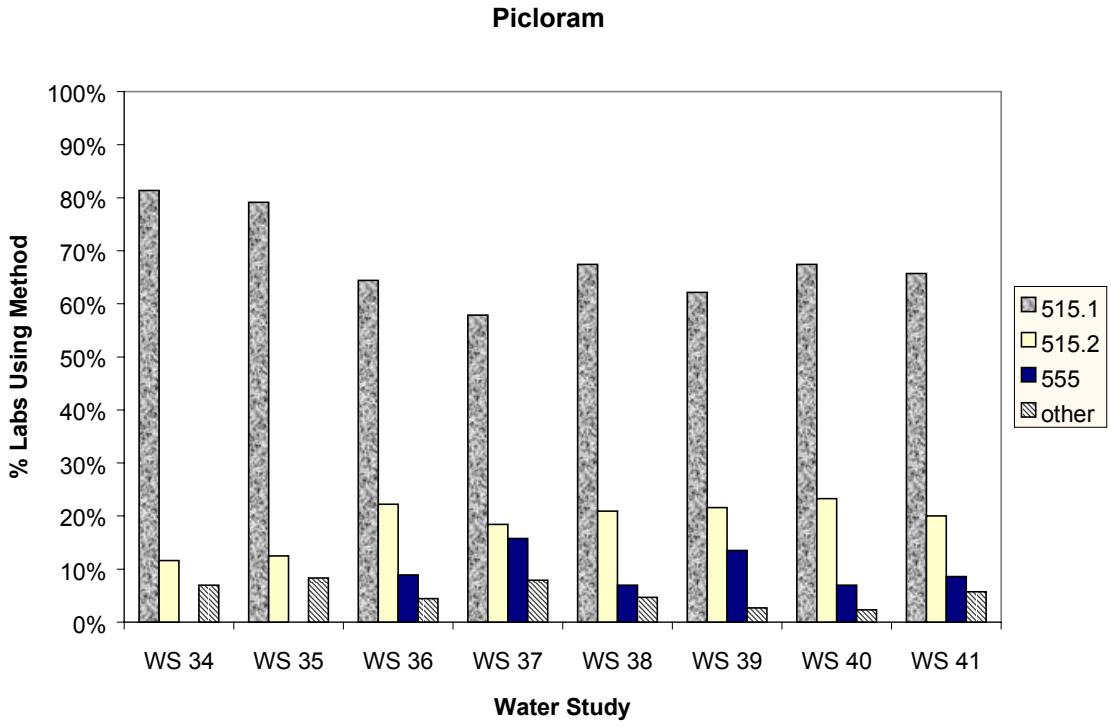
◊ EDL = estimated detection limit, used to approximate the MDL.

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of analytical methods used during each water study from WS 34 to 41 were plotted (Figure 37). The "other" techniques represent methods which were not specifically identified by participating laboratories or were otherwise unknown. As shown in Figure 37, during WS 34 to 36, the majority of laboratories used EPA 515.1 for determination of picloram. Use of EPA 515.2 gradually increased over this period but was still greatly outweighed by use of EPA 515.1. Laboratories employed EPA 555 only minimally.

Figure 37. Distribution of Analytical Techniques by WS Study: Picloram



b. Results of the PQL Analysis

The original PQL for picloram of 1.0 µg/L was derived by multiplying the detection limit (DL) by a factor of 10 (57 FR 31776). With the availability of more recent PE data, a reassessment of the PQL was attempted. Table 63 summarizes the data from WS 24 to 41 (with the exception of WS 25, 27, 28, and 29, which lacked data), indicating the study number, the true value of the WS sample, the number of results from EPA and State laboratories, and the percentage of laboratories whose results successfully passed within the acceptance limits for picloram. These limits (±2*S.D.) are not fixed but essentially represent a function of the true value (40 CFR §141.24(h)(19)(i)).

Table 63. Evaluation of Picloram Data from WS Studies Using the ± 2* S.D. Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 2* S.D. Acceptance Limits
26b	1.33	11	63.6
24b	2.63	12	91.7
32	10.6	32	93.8
34	13.2	43	93.0
33	17.4	24	100
24a	17.5	11	100
30	22.4	26	88.5
37	23.3	38	100
31	26.7	12	91.7
26a	31.2	12	91.7
36	42.2	45	100
40	44.0	43	95.3
38	56.4	43	93.0
41	62.1	35	97.1
35	62.5	24	79.2
39	74.9	37	100

As shown by Table 63, participating EPA and State laboratories in every water study but one (WS 26b) achieved a passing rate above the 75 percent criterion for determination of the PQL. Therefore, estimation of the PQL is likely to not be meaningful for this dataset. In addition, the entire range of true values for this contaminant exceeded the current PQL, some by nearly two orders of magnitude, preventing any assertions on the appropriateness of a lower PQL.

Conclusion for Picloram

The available WS data do not support a reassessment of the PQL based on the 75 percent criterion because the passing rates of laboratories almost always exceeded this value. Therefore, a quantitative reassessment of the PQL could not be performed using the graphical approach. The current PQL of 1 µg/L appears to still be appropriate.

Tetrachloroethylene

Results of the Method Comparison

The final January 1991 NPDWR for Phase II VOCs (56 FR 3526) approved several analytical methods for tetrachloroethylene. These included EPA Methods 502.1, 502.2, 503.1, 524.1, and 524.2. Since this regulation was promulgated, the Agency retained EPA Methods 502.2 and 524.2 for determination of tetrachloroethylene and introduced a new GC variation, EPA Method 551.1. Table 64 summarizes the MDLs for both the original and currently approved versions of the methods. As shown in Table 64, EPA Methods 502.2 and 551.1 have greater detection sensitivity than EPA 524.2.

Table 64. Results of the Analytical Methods Comparison for Tetrachloroethylene (Newly Promulgated Methods in Bold)

MCL = 5 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limits† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.001	EPA 502.2[2]	Purge and Trap GC	0.04 - 0.05*
EPA 502.2[1]	Purge and Trap GC	0.02 - 0.04*	EPA 524.2[2]	GC/MS	0.14
EPA 503.1[1]	Purge and Trap GC	0.01	**EPA 551.1[2]**	**LLE/GC with ECD**	0.002
EPA 524.1[1]	GC/MS	0.3			
EPA 524.2[1]	GC/MS	0.14			

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

▲ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17).

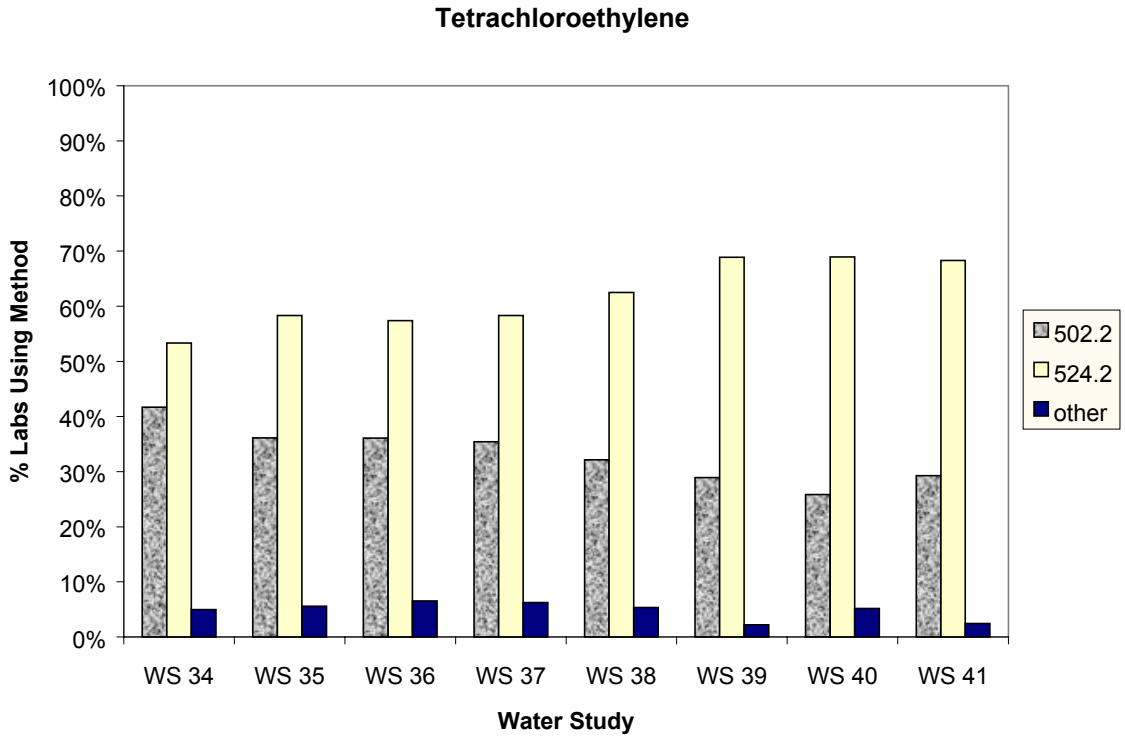
† Acceptance limits for VOCs are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the different methods used by EPA and State laboratories during WS studies 34 to 41 are shown in Figure 38. The category of "other" contains those methods that were unknown or unidentified by the participating laboratories. During WS 34 to 41, EPA 524.2 was the favored method for determining tetrachloroethylene among participating laboratories. Use of EPA 524.2 generally increased slightly over time while usage of EPA 502.2 declined. No use of EPA 551.1 was observed during these studies.

Figure 38. Distribution of Analytical Techniques by WS Study: Tetrachloroethylene



b. Results of the PQL Analysis

The Agency set the original PQL at 5 µg/L (52 FR 25700 and 56 FR 3526) for all VOCs except vinyl chloride. More recent data from WS 27 through 41 (except WS 28 which had no available data) were used to re-evaluate the PQL for tetrachloroethylene. Table 65 summarizes the results of these WS studies providing the study number, the spiked value for the WS sample, the number of laboratory results reported, and the percent of laboratories passing the WS proficiency test for tetrachloroethylene within the acceptance limits of ± 20 percent for a true value greater than10 µg/L, or ± 40 percent for a true value less than 10 µg/L (specified at 141.24(f)(17)(i)).

Table 65. Evaluation of Tetrachloroethylene Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
32	7.43	63		100
39	7.60	45		97.8
27	7.76	35		100
30	9.00	60		100
37	9.60	48		100
41	11.5	41	92.7	
31	11.6	33	97.0	
35	11.6	36	91.7	
33	12.9	34	91.2	
38	14.1	56	94.6	
40	14.7	58	91.4	
29	15.6	34	85.3	
34	16.5	60	96.7	
36	18.5	61	91.8	

The data for tetrachloroethylene could not be used to re-evaluate the PQL because State and EPA laboratories, on average, passed the performance evaluation at a rate over 90 percent. Thus, laboratories surpassed the standard 75 percent acceptance criterion typically used to determine the PQL. In addition, the true value concentrations observed in the available WS data were all greater than the current PQL of 5 µg/L. At concentrations close to the current PQL (7.43, 7.60 and 7.76 µg/L), the passing rates were 100, 98 and 100 percent, respectively. This data suggest that the current PQL of 5 µg/L could be lower.

Conclusion for Tetrachloroethylene

The method comparison results show that since the promulgation of analytical methods for tetrachloroethylene under the NPDWR, one method was retained (EPA 524.2) and two methods were added (EPA Methods 502.2 and 551.1). The most commonly used method in recent WS studies has been EPA 524.2, which is also the least sensitive method of the past and present methods. The MDL and method usage information together imply that observable analytical sensitivities for this contaminant have not improved since the promulgation of the Phase I rule. This conclusion is further supported by the observation that EPA 551.1, the most sensitive of the three currently approved methods, appears from the WS data to not be employed by EPA or State laboratories. Evaluation of the quantitative PE data showed that the majority of the laboratories conducting WS analyses had surpassed the 75 percent criterion. The high percentage of laboratories passing and high true value concentrations apparent in the WS data prevented a re-evaluation of the PQL using the graphical approach. However, the high laboratory passing rates at concentrations slightly above the current PQL may suggest that the PQL could be lower.

Thallium

Results of the Method Comparison

With the Phase V IOCs (57 FR 31776), Furnace Atomic Absorption (Furnace AA; EPA 279.2), Inductively Coupled Plasma (ICP)/MS (EPA 200.8), and Platform Furnace AA Spectrometry (EPA 200.9) were the approved methods listed for analysis of thallium in drinking water. Since this regulation was promulgated, the only change in approved analytical methods made by the Agency was the removal of EPA 279.2 from the list of approved analytical methods. MDLs for EPA Methods 200.8 and 200.9 have not changed, as indicated in Table 66. This table also shows that the discontinued EPA 279.2 was less sensitive than EPA Methods 200.8 and 200.9, meaning that the collective methods approved since promulgation are, on average, more sensitive than the methods approved at the time of promulgation. EPA 200.8 is approximately twice as sensitive than the other currently approved method, EPA 200.9.

Table 66. Results of the Analytical Methods Comparison for Thallium

MCL = 2 µg/L	Current PQL = 2 µg/L		DL▲ = 0.3 - 0.7 µg/L		Acceptance Limit† = ± 30%
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 279.2 [1]	Furnace AA	1.0	EPA 200.8[2]	ICP/MS	0.30
EPA 200.8[1]	ICP/MS (Platform)	0.30	EPA 200.9[2]	Furnace AA Spectrometry	0.70
EPA 200.9[1]	Furnace AA Spectrometry (Platform)	0.70			

[1] "Methods for Chemical Analysis of Water and Wastes (MCAWW)," EPA/600/4-79-020, March 1983.

[2] "Methods for the Determination of Metals in Environmental Samples--Supplement I," EPA/600/R-94/111, May 1994.

▲ Regulatory DLs for inorganic compounds are listed at 40 CFR §141.23(a)(4)(i) and depend on analytical methodology.

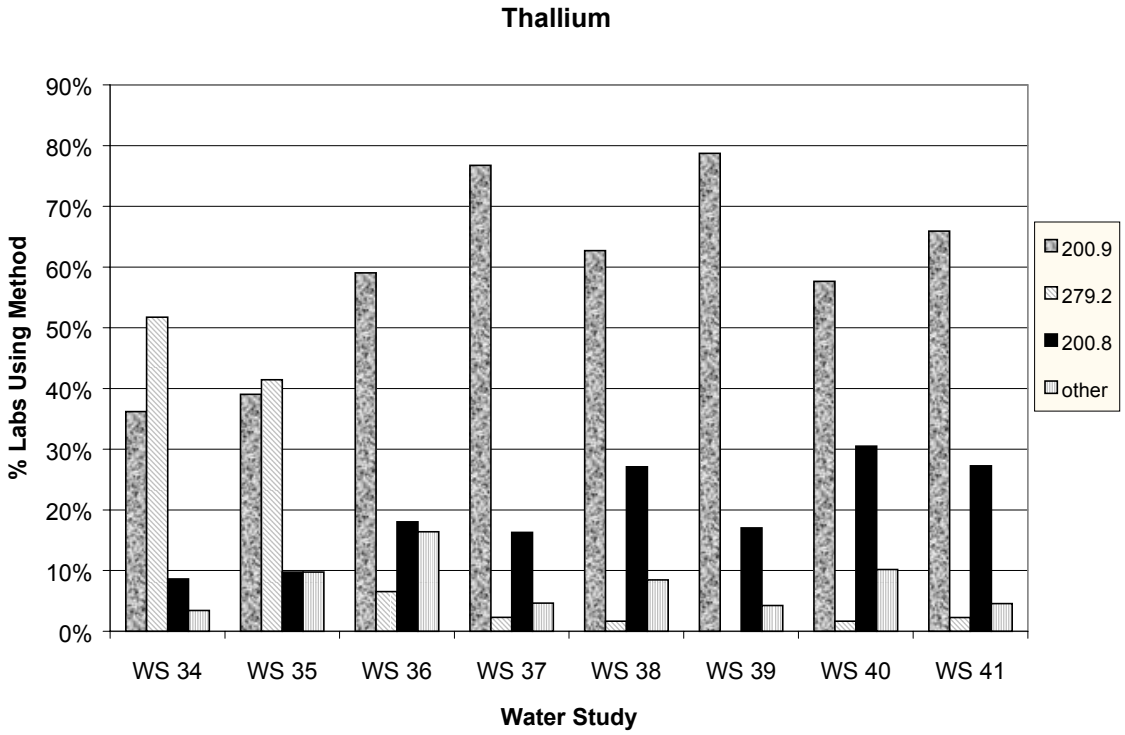
† Acceptance limits are listed at 40 CFR §141.23(k)(3)(ii).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 39 shows the variety of analytical techniques used by EPA and State laboratories in WS studies 34 to 41. The results for "other" techniques in this figure include the use of any other technique identified by the laboratories participating in the WS study, as well as "unknown" methods, i.e., techniques for which laboratories did not report the type of method used. In recent years, method usage by laboratories participating in the water studies has been dominated by EPA 200.9 (Furnace AA) which is actually less sensitive than the other approved method, EPA 200.8 (ICP/MS).

Figure 39. Distribution of Analytical Techniques by WS Study: Thallium



b. Results of the PQL Analysis

The current PQL (2 µg/L) was originally set using PE data from WS 24 through 27. For the PQL re-evaluation, data were taken from WS 24 to 41 (57 FR 31801). Table 67 summarizes the results of these water studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, and the results evaluated using acceptance limits of ± 30 percent (specified at 141.23(k)(3)(ii)).

Table 67. Evaluation of Thallium Data from WS Studies Using the 30% Acceptance Limits (In Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 30% Acceptance Limit
31	1.44	27	82
24a	2.00	30	80
37	2.38	43	91

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 30% Acceptance Limit
32	2.56	60	88
25b	3.00	21	81
41	3.50	44	96
26	4.00	37	87
36	4.50	61	98
30	5.30	48	92
39	5.60	47	98
34	6.19	58	97
35	8.00	41	93
38	8.91	59	95
33	9.56	32	91
29	9.74	21	95
40	10.0	59	98
24b	18.0	35	89
27	26.9	23	91
25a	36.0	26	96

Using the 75 percent criterion, EPA and regional laboratories were able to achieve acceptable results within the ± 30 percent acceptance window over the entire range of tested concentrations, i.e., 1.4 to 36 µg/L. Upon examination of the data, the current PQL of 2 µg/L appears to be easily supportable, as over 75 percent of laboratories successfully passed within the acceptance limits when tested at those concentration. It might even be possible for the labs to pass at a slightly lower concentration; however, a conclusion is uncertain in the absence of additional data below the PQL concentrations.

Conclusion for Thallium

The method comparison results indicate that use of the least sensitive method was discontinued since promulgation of NPDWRs. In addition, the MDLs of all the possible methods do not differ much between themselves (only by about a factor of two) with the ICP/MS method having greater sensitivity. The method usage over time shows that EPA 200.9, the less sensitive method, was the preferred choice for EPA and State laboratories. Based on the evaluation of

more recent quantitative PE data, the current PQL of 2 µg/L using a ± 30 percent acceptance limit appears to still be supportable and appropriate. Data do suggest that it may possible for the labs to pass at a slightly lower concentration.

Toxaphene

Results of the Method Comparison

At the promulgation of the NPDWRs for Phase II SOCs, three GC methods, EPA 505 (GC with microextraction), EPA 508 (GC with ECD), and EPA 525.1 (GC/MS with LSE), were approved for the determination of toxaphene in drinking water (56 FR 3552). Since that time, EPA has approved two additional GC and GC/MS methods, respectively: EPA Methods 508.1 and 525.2 (both featuring LSE extraction). Table 68 provides a summary of MDLs for the approved methods. As shown in Table 68, EPA 508 does not specify the MDL for toxaphene. The MDL for EPA 525.2 is comparable to that of EPA 505. The MDL of EPA 505 has not changed over time, 1 µg/L. The MDLs of the newer methods range from about 0.03 to 1.7 µg/L. The most sensitive method currently available, EPA 508.1, has about thirty times the sensitivity of EPA 505.

Table 68. Results of the Analytical Methods Comparison for Toxaphene (Newly Promulgated Methods in Bold)

MCL = 3 µg/L	Current PQL = 3 µg/L		DL‘ = 1 µg/L	Acceptance Limit† = ± 45%	
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 505[1]	Microextraction, GC	1	EPA 505[2]	Microextraction, GC	1
EPA 508[1]	GC with ECD	No data	EPA 508[2]	GC with ECD	No data
EPA 525.1[1]	GC/MS with LSE	7.8 - 15*	**EPA 508.1[2]**	GC with LSE, ECD	0.029
			EPA 525.2[2]	GC/MS with LSE	1.0 - 1.7*

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation, and/or laboratory/analyst performance.

‘ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(h)(18).

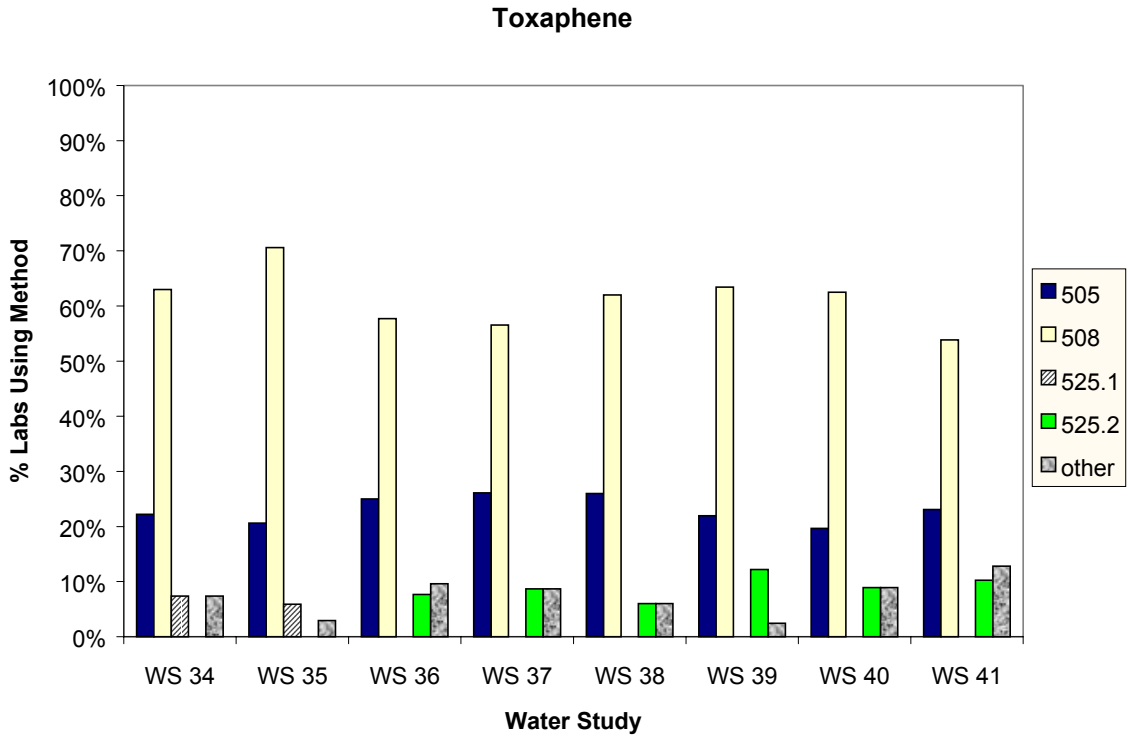
† Acceptance limits for organic compounds are listed at 40 CFR § 141.24(h)(19)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 40 illustrates the methods chosen by EPA and State laboratories for toxaphene analysis during WS PE studies 34 to 41. The category of "other" includes any unidentified or unreported techniques used by participating laboratories. As shown in Figure 40, the predominant method used by laboratories participating in the WS studies was EPA 508, followed by EPA 505. Other methods such as EPA Methods 525.1, 525.2, and other unidentified methods were used intermittently throughout WS 34 to 41. EPA 508.1 was not used by laboratories according to the PE data.

Figure 40. Distribution of Analytical Techniques by WS Study: Toxaphene



b. Results of the PQL Analysis

The current PQL of 3 µg/L was derived by multiplying the IMDL by factor of five (56 FR 3526). With the availability of more recent WS data, EPA reviewed the data from WS studies 24 to 41 to attempt a PQL re-evaluation. Table 69 summarizes each WS result including the spiked (or "true") value, the number of participating laboratories, and the percentage of laboratories passing within the specified acceptance limit for toxaphene (± 45 percent as designated in 40 CFR §141.24(h)(19)(i)).

Table 69. Evaluation of Toxaphene Data from WS Studies Using the 45% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 45% Acceptance Limits
25b	1.41	35	97.1
24b	2.33	59	91.5
30	2.80	54	92.6
31	3.31	31	93.5
39	3.65	41	92.7
26b	3.68	58	94.8
32	3.71	56	92.9
25a	4.22	35	94.3
34	5.37	54	94.4
27	6.39	34	91.2
41	6.90	39	92.3
24a	7.58	60	91.7
29	7.60	33	97.0
37	8.81	46	87.0
33	9.23	33	90.9
26a	10.8	58	96.6
38	12.7	50	92.0
36	14.7	52	90.4
40	16.5	56	94.6
35	18.3	34	97.1

EPA prefers to evaluate the PQL as the concentration at which 75 percent of laboratories are able to pass the proficiency exam within the 45 percent acceptance limits. In the case of toxaphene, however, this approach could not be used, since the percentage of laboratories passing within acceptance limits was well above the 75 percent criterion. Also, very few WS studies (e.g., 24b, 25b and 30) involved true value concentrations near the current PQL; all other studies involved spiked values above 3 µg/L. Because of these data limitations, the PQL could

not be re-evaluated using the historical linear regression approach. However, the observed high success rates of laboratories suggests that the PQL may be lowered. Since 97 percent of participating laboratories, on average, were able to determine concentrations at about half of the existing PQL, this success rate suggests that a lower PQL probably would not challenge most laboratories' analytical capabilities.

Conclusion for Toxaphene

The 1991 NPDWR for toxaphene approved the use of EPA Methods 505, 508, and 525.1 for toxaphene determination in drinking water. EPA Methods 508.1 and 525.2, using similar GC technologies, were approved more recently. The MDL of EPA 508.1 was the most sensitive compared to all other methods; however, data on method usage over time revealed that this method was not employed by laboratories. Instead, laboratories participating in the PE studies used EPA Method 508 with the greatest frequency. Unfortunately, no data are available regarding the MDL of this method. A PQL re-evaluation could not be completed due to the high success rates (well above the 75 percent criterion) in each water study as well as the high spiked concentrations in all but three water studies. The high success rates of laboratories during PE testing at concentrations well below the current PQL leads to the inference that a lower PQL would not greatly lessen laboratory performance.

1,1,1-Trichloroethane

Results of the Method Comparison

The NPDWRs for 1,1,1-trichloroethane approved certain analytical methods for the determination of this contaminant (52 FR 25690) and seven other Phase I VOCs. These methods included EPA Methods 502.1, 502.2, 503.1, 542.1, and 524.2. Since this regulation was promulgated, the Agency retained EPA Methods 502.2 and 524.2 for determination of 1,1,1-trichloroethane and introduced a new GC variation, EPA 551.1, LLE/GC with ECD. Table 70 summarizes the MDLs for both the original and current methods.

Table 70. Results of the Analytical Methods Comparison for 1,1,1-Trichloroethane (Newly Promulgated Methods in Bold)

MCL = 200 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL◊ (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.003	EPA 502.2[2]	Purge and Trap GC	0.01 - 0.03*
EPA 502.2[1]	Purge and Trap GC	0.03	EPA 524.2[2]	GC/MS	0.04 - 0.08*
EPA 524.1[1]	GC/MS	0.3	**EPA 551.1[2]**	LLE/GC with ECD	0.005
EPA 524.2[1]	GC/MS	0.08			

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

▲Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17)(i).

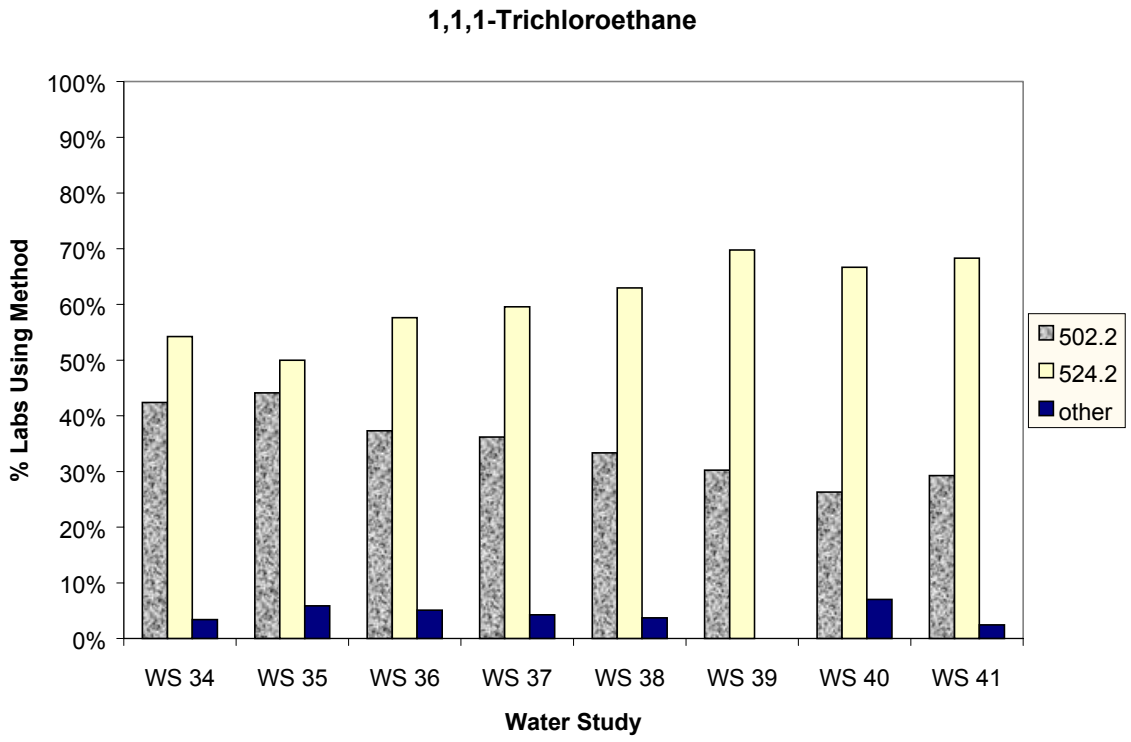
†Acceptance limits are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of the different methods used by the EPA and State laboratories during WS studies 34 to 41 are shown in Figure 41. The category of "other" contains those methods that were unknown or unidentified by the participating laboratories. As shown in Figure 41, the increase in EPA and State laboratory usage of EPA 524.2 was accompanied by a gradual decrease in use of EPA 502.2 during WS 34 to 41. Although EPA 551.1 was approved during this time, laboratories participating in WS studies did not report usage of this method.

Figure 41. Distribution of Analytical Techniques by WS Study: 1,1,1-Trichloroethane



b. Results of the PQL Analysis

As with the majority of the Phase I VOCs, the current PQL for 1,1,1-trichloroethane of 5 µg/L was determined using a multiplier of ten times the detection limit of 0.5 µg/L (52 FR 25700). Re-evaluation of the PQL was attempted using data from WS studies 24 through 41. Table 71 summarizes the results of these WS studies, providing the study number, the spiked value for the WS sample, the number of laboratory results, and the percent of laboratories passing the WS proficiency test for 1,1,1-trichloroethane within the specified acceptance limits (± 20 percent for true values greater than10 µg/L and ± 40 percent for true values less than 10 µg/L as specified at 141.24(f)(17)(i)).

Table 71. Evaluation of 1,1,1-Trichloroethane Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
24	3.21	57		98.2
34	5.73	59		100
30	7.13	59		98.3
40	7.20	57		98.2
27	7.38	37		97.3
35	8.78	34		100
29	8.80	35		100
32	10.1	62	95.2	
37	10.3	47	87.2	
39	11.2	43	90.7	
25	11.3	37	83.8	
41	12.6	41	100	
31	13.0	36	100	
26	13.6	59	86.4	
36	14.5	59	100	
33	14.6	33	87.9	
38	17.2	54	96.3	

The 1,1,1-trichloroethane data from Table 71 are insufficient for a PQL re-evaluation using the graphical or linear regression approach. The high laboratory passing rates do not permit evaluation of the PQL using the 75 percent criterion. In addition, only one spike concentration (WS 24) was below the current PQL of 5 µg/L. However, the laboratory passing rates at spike concentrations around the current PQL exceeded 98 percent. This information suggests that a lower PQL could be possible.

Conclusion for 1,1,1-Trichloroethane

The method comparison results show that since the promulgation of analytical methods under the NPDWR, EPA Methods 502.2 and 524.2 have remained in use whereas EPA 551.1 was more recently approved. While EPA 551.1 is the most sensitive of the three currently approved methods, this method is not currently used by EPA or State laboratories according to the available WS data. However, all current methods are more sensitive than the methods approved at promulgation, as shown in Table 70. Evaluation of the quantitative PE data showed that the majority of the laboratories conducting WS analyses were able to surpass the 75 percent criterion needed to evaluate the PQL. Because of the high percentage of laboratories passing and an insufficient number of spike concentrations below the 5 µg/L, a re-evaluation of the PQL could not be performed using the graphical approach. However, the available data do suggest that the PQL could be lower.

1,1,2-Trichloroethane

Results of the Method Comparison

As determined by the Phase I rules for volatile organic compounds (57 FR 31776), the approved methods listed for analysis of 1,1,2-trichloroethane in drinking water were purge and trap GC and GC/MS. Since this regulation was promulgated, the detection capability of EPA Method 524.2 have become slightly more sensitive. One new analytical method, LLE/GC with ECD (EPA 551.1), has been approved by the EPA since the promulgation of the original methods. As shown in Table 72, all three currently approved methods have comparable MDLs. However, EPA 502.1, which is no longer approved for analysis, has the greatest sensitivity level of all the approved methods, past and present.

Table 72. Results of the Analytical Methods Comparison for 1,1,2-Trichloroethane (New Methods in Bold)

MCL = 5 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL◊ (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.007	EPA 502.2[2]	Purge and Trap GC	0.03
EPA 502.2[1]	Purge and Trap GC	ND °	EPA 524.2[2]	GC/MS	0.01 - 0.03*
EPA 524.1[1]	GC/MS	unknown	**EPA 551.1[2]**	LLE/GC with ECD	0.012 - 0.017*
EPA 524.2[1]	GC/MS	0.10			

[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.

[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.

◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.

* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.

▲ Regulatory DLs for organic compounds are listed at 40 CFR §141.24(f)(17)(i).

† Acceptance limits are listed at 40 CFR §141.24(f)(17)(i).

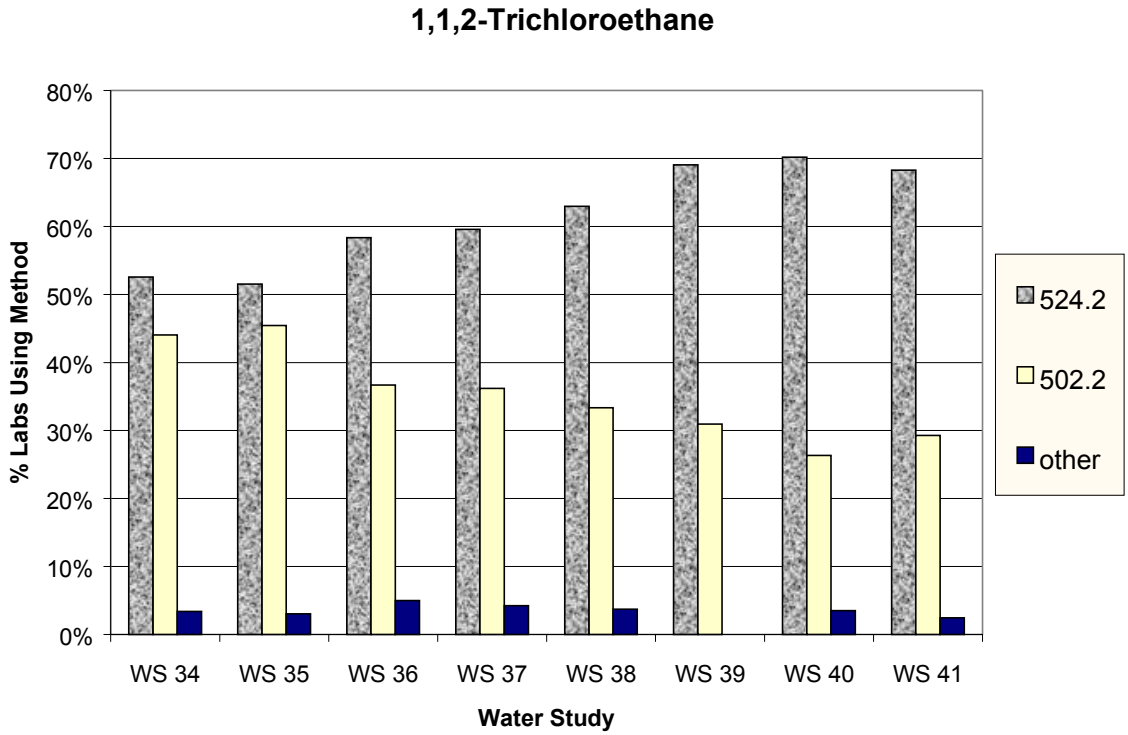
° Not determined

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 42 shows the distribution of methods used by the EPA and State laboratories during WS 34 to 41. The category of "other" includes any unknown or unreported techniques used by the participating laboratories. As shown in Figure 42, the predominant methods used since the time of promulgation are EPA Methods 524.2 and 502.2. Although EPA approved a new method (EPA 551.1), none of the laboratories that responded used it for analysis.

Figure 42. Distribution of Analytical Techniques by WS Study: 1,1,2-Trichloroethane



b. Results of the PQL analysis

The original PQL for 1,1,2-trichloroethane was estimated from PE data (specifically WS 20, 23, and 26) to be 5 µg/L (55 FR 30414). The PQL re-evaluation data were taken from WS 24 through 41 (note that data were not available for WS 24, 25, 27 to 29, and 31). Table 73 summarizes the results of these studies, including the study number, the spiked (or "true") value for the sample, the number of laboratory results, and the percent of laboratories passing the WS proficiency test for 1,1,2-trichloroethane within the specified acceptance limits (± 20 percent for a spiked value of >10 µg/L and ± 40 percent for a spiked value of <10 µg/L, as stipulated in 40 CFR §141.23(f)(17)(i)).

Table 73. Evaluation of 1,1,2-Trichloroethane Data from WS Studies Using Either 20% or 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
36	6.46	59		98.3
34	8.50	59		100
37	10.7	47	89.4	
30	11.5	50	94.0	
39	12.3	42	97.6	
35	12.8	35	90.9	
32	13.2	51	90.6	
41	13.3	40	95.1	
33	15.7	34	91.4	
38	16.3	54	98.1	
40	17.2	57	98.2	
26	26.9	54	94.4	

The standard approach to develop or evaluate a PQL could not be performed with 1,1,2-trichloroethane because the high laboratory passing percentage data (as shown in Table 73) does not permit the plotting of a useful linear regression line. Therefore, the re-evaluation of the PQL could not be done using these WS data. However, high laboratory passing rates at concentrations slightly above the current PQL of 5 µg/L suggest that a lower PQL may be possible.

Conclusion for 1,1,2-Trichloroethane

The method comparison shows that since the promulgation of the original analytical methods for 1,1,2-trichloroethane, one new method (EPA 551.1) has been approved for contaminant analysis. However, laboratories who responded to the WS studies primarily chose to use EPA Methods 524.2 and 502.2 rather than EPA 551.1, as shown by the plot of method usage over time. The MDL for 524.2 has decreased slightly over time, indicating slightly greater sensitivity. While EPA 502.1 had a maximum MDL of 0.007 µg/L, the lowest of any methods, it is currently not approved for 1,1,2-trichloroethane analyses. The evaluation of the WS data show that the majority of participating labs surpassed the 75 percent EPA criterion. Hence, because of the high percentage of labs passing and the lack of spike concentrations below the current PQL, a re-evaluation of the PQL could not be performed using linear regression or graphical analysis.

However, the high passing rates at concentrations slightly above 5 µg/L are suggestive of a potential change in the current PQL.

Trichloroethylene

Results of the Method Comparison

The analytical methods approved for the determination of trichloroethylene under the NPDWRs for Phase I VOCs include EPA Methods 502.1, 502.2, 524.1, and 524.2 (52 FR 25899). Since the promulgation of the rule in 1987, the Agency has added EPA 551.1, a GC method with liquid-liquid extraction (LLE) and electron capture detector, to the list of approved methods. The currently approved methods for trichloroethylene determination are EPA Methods 502.2, 524.2, and 551.1. Table 74 summarizes the MDLs for both the original and current approved versions of the methods. As shown in the Table the current methods are more sensitive than the past methods.

Table 74. Results of the Analytical Methods Comparison for Trichloroethylene (Newly Promulgated Methods in Bold)

MCL = 5 µg/L Current PQL = 5 µg/L DL▲ = 0.5 µg/L Acceptance Limit† = ± 20% (>10 µg/L) or ± 40% (<10 µg/L)					
Methods Approved At Promulgation			**Currently Approved Methods (141.24)**		
Method	**Technique**	**MDL◊ (µg/L)**	**Method**	**Technique**	**MDL (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.001	EPA 502.2[2]	Purge and Trap GC	0.01 - 0.4*
EPA 502.2[1]	Purge and Trap GC	0.06	EPA 524.2[2]	GC/MS	0.02 - 0.19*
EPA 503.1[1]	Purge and Trap GC	0.01	**EPA 551.1[2]**	LLE/GC with ECD	0.002
EPA 524.1[1]	GC/MS	0.4			
EPA 524.2[1]	GC/MS	0.02			

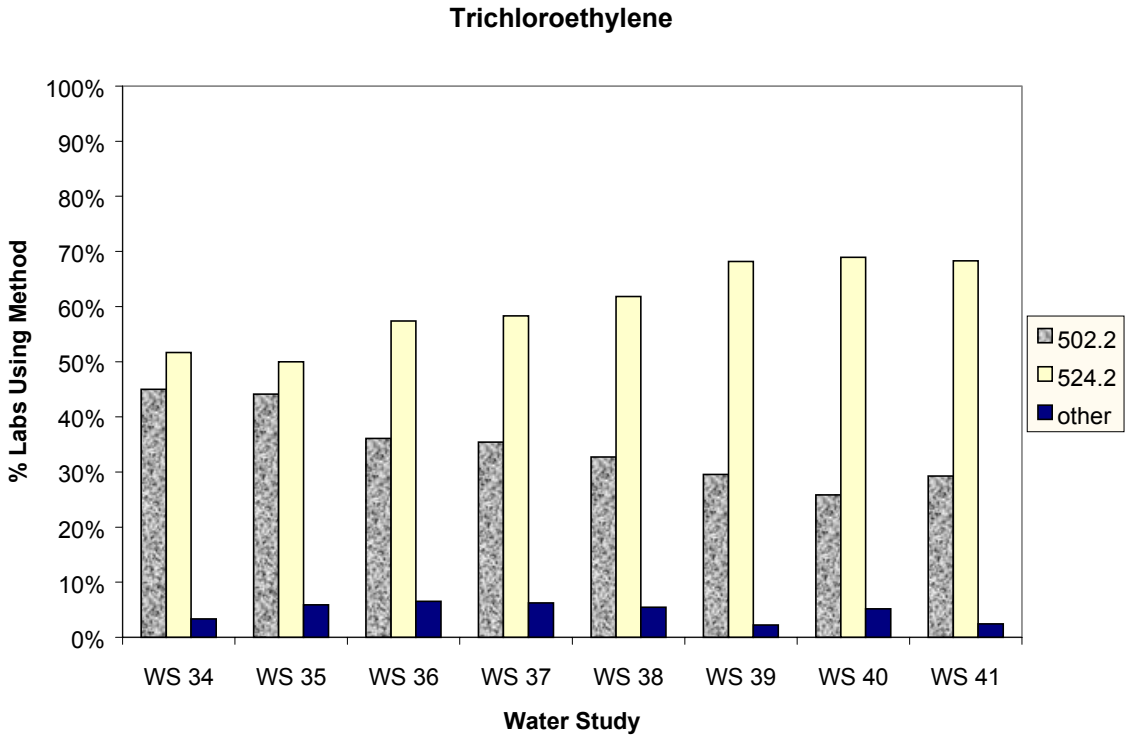
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17)(i).
† Acceptance limits for VOCs are listed at 40 CFR § 141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

Figure 43 shows the distribution of the different methods used by the EPA and State laboratories during WS studies 34 to 41. The category of "other" contains those methods that were unknown or unidentified by the participating laboratories. As shown in Figure 43, laboratories participating in studies WS 34 to 41 used EPA 524.2 with increasing frequency over EPA 502.2. No laboratories used EPA 551.1 for PE determinations of trichloroethylene.

Figure 43. Distribution of Analytical Techniques by WS Study: Trichloroethylene



b. Results of the PQL Analysis

The original PQL of 5 µg/L for trichloroethylene was determined by evaluation of data from WS studies 8 to 11 (50 FR 46880). For the PQL reassessment, updated data from WS 24 to 41 were reviewed. Table 75 summarizes the results of these WS studies providing the study number, the spiked value for the WS sample, the number of laboratory results, and the percent of laboratories passing the WS proficiency test for trichloroethylene within the acceptance limits (± 20 percent for a true value greater than10 µg/L, or ± 40 percent for a true value lower than 10 µg/L).

Table 75. Evaluation of Trichloroethylene Data from WS Studies Using the ± 20% or ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 20% Acceptance Limits	% Labs Passing ± 40% Acceptance Limits
40	5.80	58		98.3
35	6.13	34		97.1
26	6.63	59		100
41	6.87	41		100
24	7.36	57		100
31	7.46	36		97.2
37	8.70	48		97.9
34	8.89	60		100
30	9.45	38		100
25	10.4	37	83.8	
32	11.2	63	95.2	
38	12.4	55	94.5	
27	14.0	37	91.9	
33	14.9	34	94.1	
29	15.9	34	85.3	
39	16.4	44	95.5	
36	17.4	61	96.7	

Table 75 reveals that the percentage of laboratories passing the acceptance limit averaged over 90 percent. Because the laboratories exceeded the standard 75 percent criterion used to estimate the PQL, the typical regression method could not be successfully employed to estimate a new PQL value. Another limitation of the data was that the true value concentrations in the available studies were all greater than 0.5 µg/L, preventing evaluation of laboratory performance at concentrations below the current PQL. However, high laboratory passing rates at concentrations slightly above the current PQL of 5 µg/L suggest that a lower PQL may be possible.

Conclusion for Trichloroethylene

The method comparison results show that, since the promulgation of analytical methods under the original NPDWR for trichloroehtylene, two of these methods are no longer approved

for determination of this contaminant. While EPA 551.1 is the most sensitive of the three currently approved methods, this method is not currently used by EPA or State laboratories according to the available WS data. Instead, EPA 524.2, the least sensitive of the three current methods, has been the primary method of choice. Evaluation of the quantitative PE data shows that the majority of the laboratories conducting WS analyses had surpassed the 75 percent criterion. Because of the high percentage of laboratories passing, a re-evaluation of the PQL could not be performed using this approach. However, the high laboratory passing rates at concentrations slightly above 5 µg/L are suggestive of a change in the PQL.

Vinyl Chloride

Results of the Method Comparison

With the promulgation of NPDWRs for Phase I VOCs (proposed November 1985, 50 FR 46905; finalized July 1987, 52 FR 25690), EPA Methods 502.1, 502.2, 524.1, and 524.2 were listed as approved methods for the determination of vinyl chloride in drinking water. Since promulgation of this rule, EPA Methods 502.1 and 524.1 were removed. As shown in Table 76, the MDLs of the current methods are comparable in sensitivity to previously approved methods.

Table 76. Results of the Analytical Methods Comparison for Vinyl Chloride

MCL = 2 µg/L	**Current PQL = 2 µg/L**		**DL▲ = 0.5 µg/L**	**Acceptance Limit† = ± 40%**	
Methods Approved At Promulgation			**Currently Approved Methods**		
Method	**Technique**	**MDL◊ (µg/L)**	**Method**	**Technique**	**MDL* (µg/L)**
EPA 502.1[1]	Purge and Trap GC	0.01	EPA 502.2[2]	Purge and Trap GC	0.01 - 0.04
EPA 502.2[1]	Purge and Trap GC	0.01 - 0.18*	EPA 524.2[2]	GC/MS	0.04 - 0.17
EPA 524.1[1]	GC/MS	0.3			
EPA 524.2[1]	GC/MS	0.04			

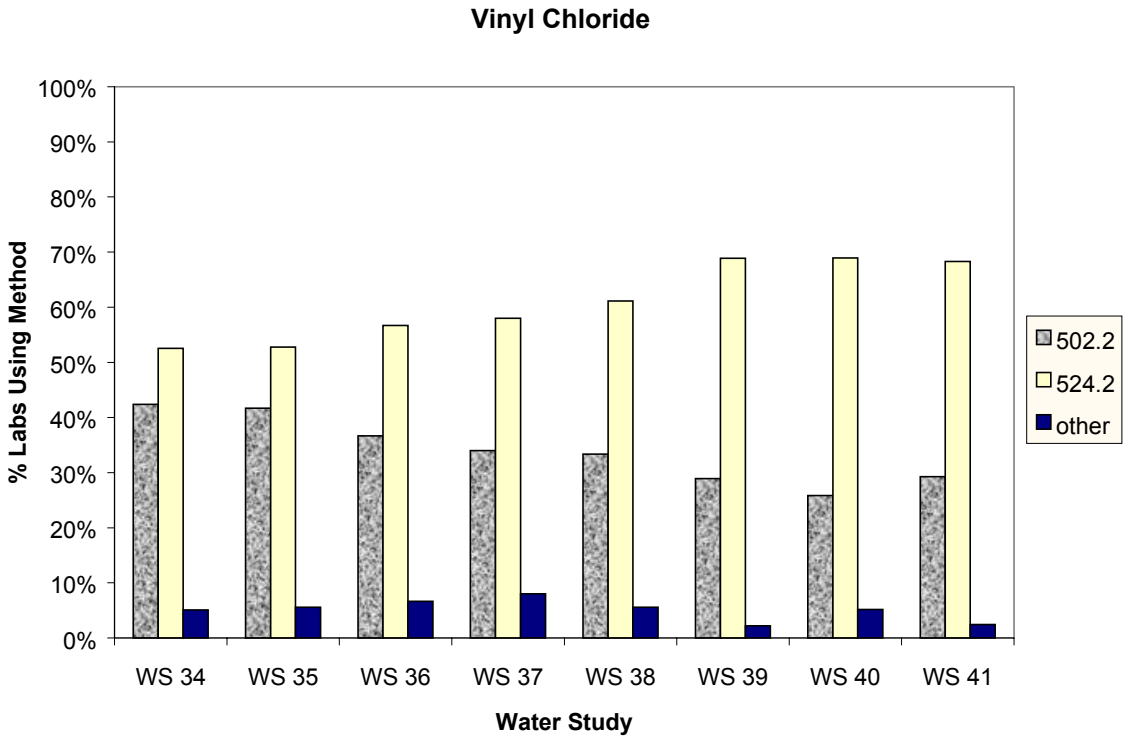
[1] "Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, December 1988.
[2] "Methods for the Determination of Organic Compounds in Drinking Water--Supplement III," EPA/600/R-95-131, August 1995.
◊ The MDLs of the original methods for this contaminant ranged from 0.2 - 0.5 µg/L according to the July 1987 Federal Register notice promulgating NPDWRs for the VOCs (52 FR 25690). However, the 1988 methods manual cited in footnote 1lists the MDLs shown above.
* Multiple method detection limit (MDL) values result from variability of reagents, instrumentation and/or laboratory/analyst performance.
▲ Regulatory DLs for organic compounds are listed at 40 CFR § 141.24(f)(17)(i).
† Acceptance limits for vinyl chloride are listed at 40 CFR §141.24(f)(17)(i).

Results of the Analysis of the WS Data

a. Method Usage Over Time

The distribution of methods used by EPA and State laboratories during WS studies 34 to 41 is plotted in Figure 44. The category of "other" contains those methods that were unknown or unidentified by the participating laboratories. As shown in Figure 44, over the course of the past eight WS Studies, the use of EPA 524.2 has grown while the use of EPA 502.2 has decreased. EPA 524.2 has consistently remained the most commonly used method for vinyl chloride determination.

Figure 44. Distribution of Analytical Techniques by WS Study: Vinyl Chloride



b. Results of the PQL Analysis

The original PQL of 2 µg/L for vinyl chloride was determined by using multi-laboratory performance data, rather than the multiplier procedure used for other VOCs (52 FR 25700). A re-evaluation of the PQL was attempted using more recent PE data from WS 24 to 41. Table 77 summarizes the results of these studies, providing the study number, the spiked value for the WS sample, the number of laboratory results, and the percentage of laboratories passing the performance evaluation within the ± 40 percent acceptance limits (40 CFR § 141.24(f)(17)(ii)).

Table 77. Evaluation of Vinyl Chloride Data from WS Studies Using ± 40% Acceptance Limits (in Order of Increasing Concentration)

WS #	Spiked "True" Value (µg/L)	# Results from EPA and State Labs	% Labs Passing ± 40% Acceptance Limits
32	2.57	43	79.1
27	3.57	39	79.5
24	4.35	57	80.7
35	4.91	36	100
30	5.48	58	82.8
39	6.19	45	91.1
33	7.35	34	79.4
26	8.70	59	86.4
36	9.47	60	88.3
31	11.9	39	79.5
25	12.4	38	86.8
34	14.1	59	93.2
29	14.6	38	78.9
37	14.8	50	88.0
38	17.9	54	96.3
41	22.3	41	92.7
40	27.2	58	94.8

EPA prefers to estimate the PQL by choosing the spiked value at which 75 percent of laboratories can determine the concentration within the appropriate 40 percent acceptance window. In the case of vinyl chloride, the results from participating laboratories listed in Table 77 could not be used to re-evaluate the PQL because the laboratory success rate exceeded this 75 percent criterion. The other limitation of these data was the high range of spiked concentrations exhibited during the WS studies, which exceeded the current PQL of 2 µg/L. Therefore, the available data do not provide sufficient data to recalculate the PQL. However, passing rates of 79 to 80 percent for the three lowest concentrations (2.57, 3.57 and 4.35 µg/L) above the current PQL of 2 µg/L suggest that the current PQL is in the appropriate range and unlikely to change.

Conclusion for Vinyl Chloride

As shown by the method comparison table, EPA Methods 502.2 and 524.2 were approved with the Phase I Rule promulgation for VOCs and continue to be approved today. The sensitivity of newer versions of the methods are comparable older versions. According to the plot of methods usage over time, the laboratories who participated in WS 34 to 41 employed EPA 524.2 more frequently than EPA 502.2. The available PE data were reviewed but did not provide sufficient data to recalculate the PQL. Evaluation of the available WS data suggest that the current PQL of 2 μg/L vinyl chloride is unlikely to change.

VI. Conclusion

As part of the 1996-2002 Six-Year Review of National Primary Drinking Water Regulations, EPA's Office of Ground Water and Drinking Water re-evaluated the analytical feasibility for 38 selected NPDWRs. Table 78 summarizes the results of the analytical feasibility analysis. Upon review, EPA found that the majority of the available WS data were insufficient for the recalculation of the PQL for many of the 38 contaminants of interest. The data were considered insufficient because either the true value of the spike concentrations used in the WS studies were above the concentration of interest and/or the percentages of labs passing exceeded the 75 percent criterion used to calculate a PQL. However, for many of the 38 contaminants, the available data were sufficient to indicate whether the PQL might change or if the current PQL is still appropriate. Of the 38 NPDWRs evaluated, the available information indicates that the PQL for 23 may possibly be lower. The PQL for the remaining 15 appears to still be appropriate.

For the 23 analytes where the WS data indicate that a lower PQL may exist, EPA used the information about method usage over time, the MDLs for these methods, and the 10 x MDL multiplier to estimate what the potentially lower PQL might be. These estimates are shown in Appendix A. Pending the outcome of the health effects review, the majority of these estimated values will be used as thresholds in the occurrence and exposure analyses to determine whether an improvement in public health protection might be possible if EPA were to consider gathering more definitive data to recalculate the PQL and possibly lower the MCL.

Table 78. Summary of Results from the Methods Comparison and WS Analysis

SDWA Chemical Contaminant		Current PQL (mg/L) *(PQL at the time of the original promulgation)*	Result of the Six-Year Analytical Feasibility Reassessment
1	Alachlor	0.002	Current PQL still appropriate
2	Benzene	0.005	WS Data indicative of change
3	Benzo(a)pyrene	0.0002	Current PQL still appropriate
4	Beryllium	0.001	Current PQL still appropriate
5	Bis (2-ethylhexyl)phthalate (also known as Di(2-ethylhexyl) phthalate or DEHP)	0.006	Current PQL still appropriate
6	Cadmium	0.002	WS Data indicative of a change
7	Carbofuran	0.007	WS Data indicative of a change
8	Carbon tetrachloride	0.005	WS Data indicative of change
9	Chlordane	0.002	WS Data indicative of change
10	Chromium (total - Cr III and VI)	0.01	Current PQL still appropriate
11	1,2-Dibromo-3-chloropropane (DBCP)	0.0002	WS Data indicative of change
12	1,4-Dichlorobenzene (para)	0.005	WS Data indicative of a change
13	1,2-Dichloroethane	0.005	WS Data indicative of change
14	1,1-Dichloroethylene	0.005	WS Data indicative of change
15	Dichloromethane (methylene chloride)	0.005	WS Data indicative of change
16	1,2-Dichloropropane	0.005	WS Data indicative of change
17	Dioxin - 2,3,7,8-TCDD	3×10^{-8}	PQL most likely still appropriate - no data but unlikely to change since no new method approved
18	Diquat	0.004	Current PQL still appropriate
19	Ethylene dibromide	0.00005	Current PQL still appropriate
20	Fluoride	0.5	Current PQL still appropriate
21	Glyphosate	0.06	Current PQL still appropriate
22	Heptachlor	0.0004	WS Data indicative of change
23	Heptachlor epoxide	0.0002	WS Data indicative of change
24	Hexachlorobenzene	0.001	WS Data indicative of change
25	Hexachlorocyclopentadiene	0.001	WS Data indicative of change
26	Mercury	0.002	Current PQL still appropriate
27	Methoxychlor	0.01	WS Data indicative of change
28	Oxamyl	0.02	PQL could range from 0.02 to 0.04 mg/L
29	Polychlorinated biphenyls (PCBs) (as decachlorobiphenyl)	0.0005	Current PQL still appropriate
30	Pentachlorophenol	0.001	Current PQL still appropriate

Table 78. Summary of Results from the Methods Comparison and WS Analysis

SDWA Chemical Contaminant		Current PQL (mg/L) *(PQL at the time of the original promulgation)*	Result of the Six-Year Analytical Feasibility Reassessment
31	Picloram	0.001	Current PQL still appropriate
32	Tetrachloroethylene	0.005	WS Data indicative of change
33	Thallium (Non-zero MCLG = 0.0005 mg/L)	0.002	WS Data indicative of change
34	Toxaphene	0.003	WS Data indicative of change
35	1,1,1-Trichloroethane	0.005	WS Data indicative of change
36	1,1,2-Trichloroethane (Non-zero MCLG = 0.003 mg/L)	0.005	WS Data indicative of change
37	Trichloroethylene	0.005	WS Data indicative of change
38	Vinyl chloride	0.002	Current PQL still appropriate

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Appendix A

After re-evaluating more recent Water Supply data for the Six-Year Review, EPA found that insufficient data were available around the 75 percent criterion to actually recalculate the PQL. However, in many cases, the passing rates for the EPA Regional and State laboratories exceeded the 75 percent at values close to the current PQL. If the passing rates were greater than 80 to 85 percent at spike concentrations close to the current PQL, then this information was considered to be indicative of a possible change in the PQL. If data indicated a possible change in the PQL, EPA then evaluated the distribution of the analytical methods used to analyze the spike samples in the WS studies. Evaluation of the method usage over time allowed EPA to determine the analytical methods that appear to be the most widely used for the analysis of a particular contaminants. Knowledge of which analytical methods are the most widely used, along with the MDL for these methods, and a ten times MDL multiplier allowed EPA to estimate where the potential lower limit of quantitation may lie today. These values are shown in Table 79. Most of these estimated PQLs have or will be used as a threshold value in the occurrence analysis to help the Agency determine if there may be a significant gain in public health protection if EPA were to consider gathering the information needed to recalculate the PQL.

Table 79. Estimated PQLs Based on Method Usage and 10 x MDL Multiplier
Estimated values to use in the Occurrence and Exposure (O/E) analyses

	Chemical analyte	**Current PQL** (mg/L) *(PQL at the time of the original promulgation)*	**Most commonly used methods with published MDL** (mg/L)		**Estimated value for O/E** (mg/L)
1	Benzene	0.005	EPA 524.2 EPA 502.2	0.00004 (upper MDL) 0.00001	0.0004 0.0001 Use upper value of 0.0004 mg/L
2	Cadmium	0.002	EPA 200.7 EPA 200.8 EPA 200.9 all used equally	0.001 0.0005 0.00005	0.01 0.005 0.0005 If use upper or intermediate value - these are higher than current MCL. Could use 0.0005 mg/L as a value for O/E but this would probably be the lower edge of the quantitation limit.
3	Carbofuran	0.007	EPA 531.1	0.00052	0.0052 Round to 0.005 mg/L
4	Carbon tetrachloride	0.005	EPA 524.2 EPA 502.2	0.00021 0.00002	0.0021 0.0002 Use upper value of 0.0021 and since this value is close to one-half MCL, use 0.0025 mg/L.

Table 79. Estimated PQLs Based on Method Usage and 10 x MDL Multiplier
Estimated values to use in the Occurrence and Exposure (O/E) analyses

	Chemical analyte	Current PQL (mg/L) *(PQL at the time of the original promulgation)*	Most commonly used methods with published MDL (mg/L)		Estimated value for O/E (mg/L)
5	Chlordane	0.002	EPA 505 EPA 508	0.00014 0.0000041	0.0014 0.000041 Because of an order of magnitude difference between these two values, use the average and round up. Average = 0.00072 mg/L Round up to 0.001 mg/L
6	1,2-Dibromo-3-chloropropane (DBCP)	0.0002	EPA 504.1	0.00001	0.0001 mg/L
7	1,4-Dichlorobenzene (para)	0.005	EPA 502.2 EPA 524.2	0.00029 0.00004	0.0029 0.0004 Use the upper value of 0.0029 mg/L. Since close to one-half MCL, could also use 0.0025 mg/L.
8	1,2-Dichloroethane	0.005	EPA 502.2 EPA 524.2	0.00007 0.00006	0.0007 0.0006 Could use either since so close and round to 0.001 mg/L
9	1,1-Dichloroethylene	0.005	EPA 524.2 EPA 502.2	0.00012 0.00007	0.0012 0.0007 Could use either both round to 0.001 mg/L
10	Dichloromethane (methylene chloride)	0.005	EPA 524.2 EPA 502.2	0.00003 0.00002	0.0003 0.0002 Used average for these two since close to one-half MCL Average = 0.00025 mg/L
11	1,2-Dichloropropane	0.005	EPA 524.2 EPA 502.2	0.00004 0.00003	0.0004 0.0003 Use upper value 0.0004 mg/L
12	Heptachlor	0.0004	EPA 525.2 EPA 505 EPA 508	0.00015 (upper MDL) 0.000003 0.0000015	0.0015 0.00003 0.000015 Because of widespread between these - use the intermediate value and round to 0.0001 mg/L to be conservative

Table 79. Estimated PQLs Based on Method Usage and 10 x MDL Multiplier
Estimated values to use in the Occurrence and Exposure (O/E) analyses

	Chemical analyte	Current PQL (mg/L) *(PQL at the time of the original promulgation)*	Most commonly used methods with published MDL (mg/L)		Estimated value for O/E (mg/L)
13	Heptachlor epoxide	0.0002	EPA 525.2 EPA 508 EPA 505	0.00013 0.0000059 0.000004	0.0013 0.000059 0.00004 Because of widespread between these - use the intermediate value and round to 0.0001 mg/L to be conservative
14	Hexachlorobenzene	0.001	EPA 508 EPA 505 EPA 525.2	0.0000077 0.000002 0.000001	0.000077 0.00002 0.00001 Because these are close together - use upper value of 0.000077 and round up to 0.0001 mg/L
15	Hexachlorocyclopentadiene	0.001	EPA 508 EPA 505 EPA 525.2	N/A 0.00013 0.0001	----- 0.0013 (rounds to 0.001) 0.001 Use 0.001 mg/L
16	Methoxychlor	0.01	EPA 505 EPA 525.2 EPA 508	0.00096 0.0001 0.000022	0.0096 0.001 0.00022 Use intermediate value of 0.001 mg/L
17	Oxamyl	0.02	----------	----------	PQL could range from 0.02 to 0.04 mg/L
18	Tetrachloroethylene	0.005	EPA 525.2 EPA 502.2	0.00014 0.00005	0.0014 0.0005 In this case, used the lower value of 0.0005 mg/L because of the 95-100 % passing rates around the current PQL.
19	Thallium (Non-zero MCLG = 0.0005 mg/L)	0.002	EPA 200.9 EPA 200.8	0.0007 0.0003	0.007 0.003 These values higher than current MCL, could not estimate using 10 multiplier.
20	Toxaphene	0.003	EPA 508 EPA 505	N/A 0.001	---------- 0.01 (higher than current MCL)
21	1,1,1-Trichloroethane	0.005	EPA 524.2 EPA 502.2	0.00008 0.00003	0.0008 0.0003 Average = 0.0005 mg/L

Table 79. Estimated PQLs Based on Method Usage and 10 x MDL Multiplier
Estimated values to use in the Occurrence and Exposure (O/E) analyses

	Chemical analyte	**Current PQL** (mg/L) *(PQL at the time of the original promulgation)*	**Most commonly used methods with published MDL** (mg/L)		**Estimated value for O/E** (mg/L)
22	1,1,2-Trichloroethane (Non-zero MCLG = 0.003 mg/L)	0.005	EPA 524.2 EPA 502.2	0.00003 0.00003	0.0003 0.0003 Estimated value is higher than MCLG of 0.003 mg/L. So should use MCLG value as threshold in O/E analysis.
23	Trichloroethylene	0.005	EPA 502.2 EPA 524.2	0.0004 0.00019	0.004 0.0019 Average = 0.0029 mg/L This is close to one-half MCL - so use 0.0025 mg/L.